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LEVEL III

BOMB DETECTION SYSTEM STUDY

TECHNICAL REPORT

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OCTOBER 1966

by
A. Dravnieks
IIT Research Institute
Chicago, Illinois 60616
Under Contract No. FA65WA-1200

for

FEDERAL AVIATION AGENCY
AIRCRAFT DEVELOPMENT SERVICE

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Chicago, Illinois 60616

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ABSTRACT

✓ A process for detection of concealed dynamite was developed and an engineering model designed, built, and demonstrated. The process is based on detection of ethylene glycol dinitrate vapor in air. The essential steps are adsorption of the vapor on a gold surface, desorption from the gold into a short partition column, and passage through an electron-capture detector, whose response is electronically monitored. Nitrobenzene vapor was also detectable, but was distinguishable from ethylene glycol dinitrate vapor. The merits of microwave absorptometry and microwave-heated plasma emission spectrophotometry for detection of dynamite, DNT, and TNT were explored. A method for detection of black powder by characterization of its vapor was not found. ↑

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1.0 INTRODUCTION

Under Contract No. FA-WA-4782, "Bomb Detection System Study," conducted for the Federal Aviation Agency in 1964, IIT Research Institute studied the nature and the amount of characteristic vapors emitted by various explosives and estimated the feasibility of a bomb detection system that rapidly detects the characteristic vapors at high dilutions in air. These findings were summarized in Report FAA-ADS-34, "Bomb Detection System Study," issued January 1965. We concluded that detection of bombs in luggage and airplanes is feasible through detection of ethylene glycol dinitrate vapor in the case of dynamite and of dinitrotoluene vapor in the case of most military explosives and many smokeless powders, provided that there is reasonable escalation of available techniques and devices for rapid concentration of these vapors from air and that the automatic gas chromatographic analysis sequence is rapid.

The present project, Contract No. FA65WA-1200, was undertaken to explore and optimize every step and component in the sampling and analysis techniques; find means of dealing with possible interferences, especially nitrobenzene; and then utilize this experience to design and operate, under conditions of increasing difficulty, an engineering model of the bomb detector. Furthermore, means for detection of black powder were to be sought, and possible alternatives to the electron-capture detector used in the previous project were to be explored.

Consequently, the work was subdivided into four tasks: (1) optimization of the sampling and detection process variables and components, (2) exploration of other detectors and study of vapors from black powder, (3) bench-scale operation of all optimized steps to carry the detection from sampling to readout and to define the design parameters for the engineering model, and (4) design and construction of the engineering model and its demonstration under various conditions.

2.0 OPTIMIZATION OF SYSTEM VARIABLES

In the first year's work (Contract FA-WA-4782), some important factors in the detection of dynamite and other explosive vapors were uncovered and explicated. For instance, the overriding importance of the vapor pressure of the explosive components was clearly demonstrated. Also, the need for relatively short partition tubes (or columns), rather than the usual long, densely packed columns used for most chromatographic separations, was shown. These and other initial results set the stage for the more detailed studies needed to optimize the various steps of the detection process as discussed here.

The detection scheme divided into several steps. First, the vapors from air are trapped (or concentrated) on a metal surface. This, the sampling (or collection) step, is followed by injection of the trapped material into a tube coated inside with an absorbing film or loosely packed with a suitably coated powdered solid. Gas flowing through this tube serves to separate the desired vapor from air and from irrelevant contaminants picked up by the trap. This gas then carries the vapor into a detection chamber, in which the vapor upsets the previously established electrical steady-state condition. This upset is electrically detected and amplified. Finally, the electric signal is recorded in such a way that the time spent in the tube (frequently called a column) and the amount of vapor present are noted.

Some of the questions to be answered in order to optimize the detection process involve the construction materials necessary for the various steps of the vapor trapping and detection process. Other questions involve the temperatures, pressures, gas composition, and type of column best suited to detection of the characteristic vapor. Still other questions involve instrumental factors, such as the best detector cell type or design and optimum working voltage for the cell.

In the earlier work (Contract FA-WA-4782) it was found that metal surfaces were especially effective in trapping (or retaining) explosive vapors for later recovery. However, metals also tend to decompose the unstable vapors of explosives, especially at higher temperatures. Hence, the question arises as to what metal surface is most effective in trapping the vapors and yet least active in decomposing them when heated to release vapors into the separation stream. Similarly, the question as to what tubing material is best for transferring the released vapor through the column and other plumbing needs to be answered.

Time is of utmost importance in the optimization of system variables. The retention time, i.e., the time spent in the gas chromatographic column, identifies a vapor if other variables are properly controlled. The retention time is influenced by temperature, pressure, flow rate, and various column parameters, such as length, diameter, and especially the type of packing. These variables also greatly influence the shape of the signal produced by the total system.

Selection of the best detector and operating conditions is especially important for an essentially automatic system such as that proposed as the end product of the study. A stable, noise-free system optimized to be most sensitive to the vapors sought is an obvious necessity.

This section of the report discusses all the variables in detail, describes the experimental work performed to explore these, and outlines the selection of variables pertinent to an optimized detection system.

2.1 Experimental Apparatus

Several lines of investigation were carried on simultaneously by a team of workers, each investigating the various steps in the detection scheme: detector, partition tube (or column), and vapor extraction from air. To this end, three complete and independent research chromatographic systems were constructed. Figure 1 is a schematic diagram of the principal parts of this system.

Proceeding from left to right in the figure, G is a tank of pure compressed gas, the carrier gas. V_1 is a pressure-reducing valve supplying gas at 10 to 20 psig to needle valve V_2 , which allows fine control of the rate of gas flow through the system. The gas then enters an injection block, I, where it is heated and carried to the column. Inside the injection block is a tee-shaped fitting with a silicone high-temperature rubber septum at one port, to allow insertion of a syringe needle, S. When the needle is inserted, it rapidly heats to the temperature of the block. Thus any material absorbed on its surface is released. This process is called "flash vaporization."

The vapors are then carried into a separation column with packing kept in a long thermostatted copper cylinder, C. The various vapors separate in time and space by interactions with the column and finally emerge into the detector, D, placed in a heated copper cylinder. The vapors then pass into the flowmeter, F, and out to the air through the vent, V.

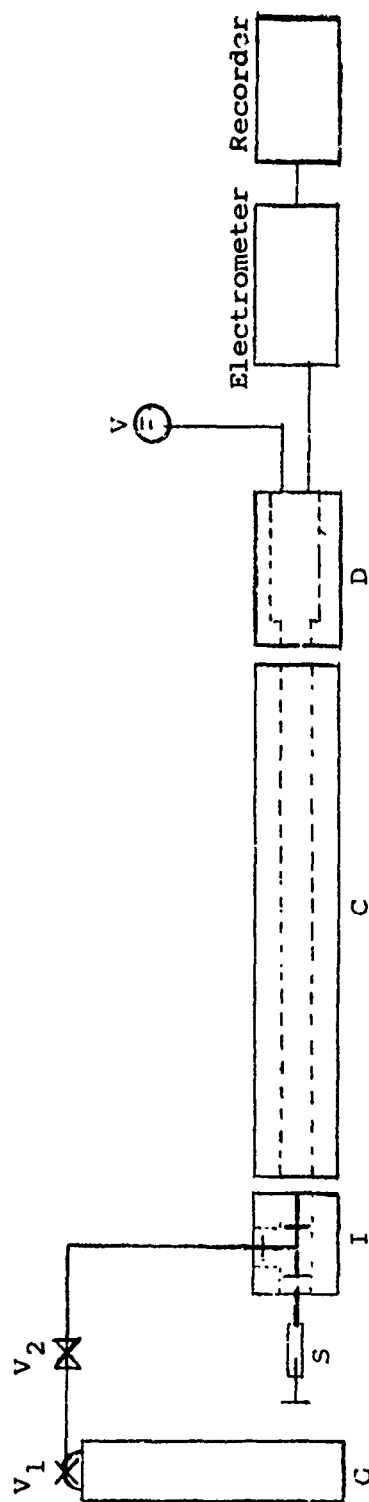


FIGURE 1 - Bench Apparatus for Studies of Detection System Variables

Disturbance of the electrical equilibrium in the detector when the vapors enter it causes a signal, which is amplified by the electrometer and sent to a strip-chart recording potentiometer. This completes the detection process.

By modification of this apparatus in various ways, all the processes necessary for bomb detection were studied on a bench laboratory scale. The following discussion concerns the optimization of variables in the detection process in this order:

- (1) Detector variables
- (2) Column and separation variables
- (3) Trapping (or collection) variables.

2.2 Electron Capture

Numerous sensitive methods for detection of vapors in gas are available, such as flame ionization, argon ionization, thermionic emission, and the older techniques of katharometry and gas-density measurements. The electron-capture (or electron-affinity) technique was chosen for development in this study mainly because it is several orders of magnitude more sensitive to the chemical vapors of importance in detection of explosives. Also, it is inherently more selective, since it is relatively insensitive to many common organic vapors, including jet fuels and other substances derived from petroleum.

2.2.1 Principles of Electron-Capture Detection

Early vapor-detection methods depended on such physical properties as thermal conductivity and density and used electrical techniques of amplification only incidentally. Recent ionization methods are based more firmly on the fundamental electrical nature of all materials. The detector becomes an active element in an electronic circuit -- somewhat analogous to an amplifier tube in a radio circuit. Because of this, much greater sensitivity (in terms of the amount of material needed to cause a measurable change in the circuit) is possible.

The electron-capture detector is essentially an ionization device in which vapors that have affinity for electrons decrease the electrical conductivity of gases. Its operation can be understood by reference to Figure 2, a schematic diagram of its essential parts.

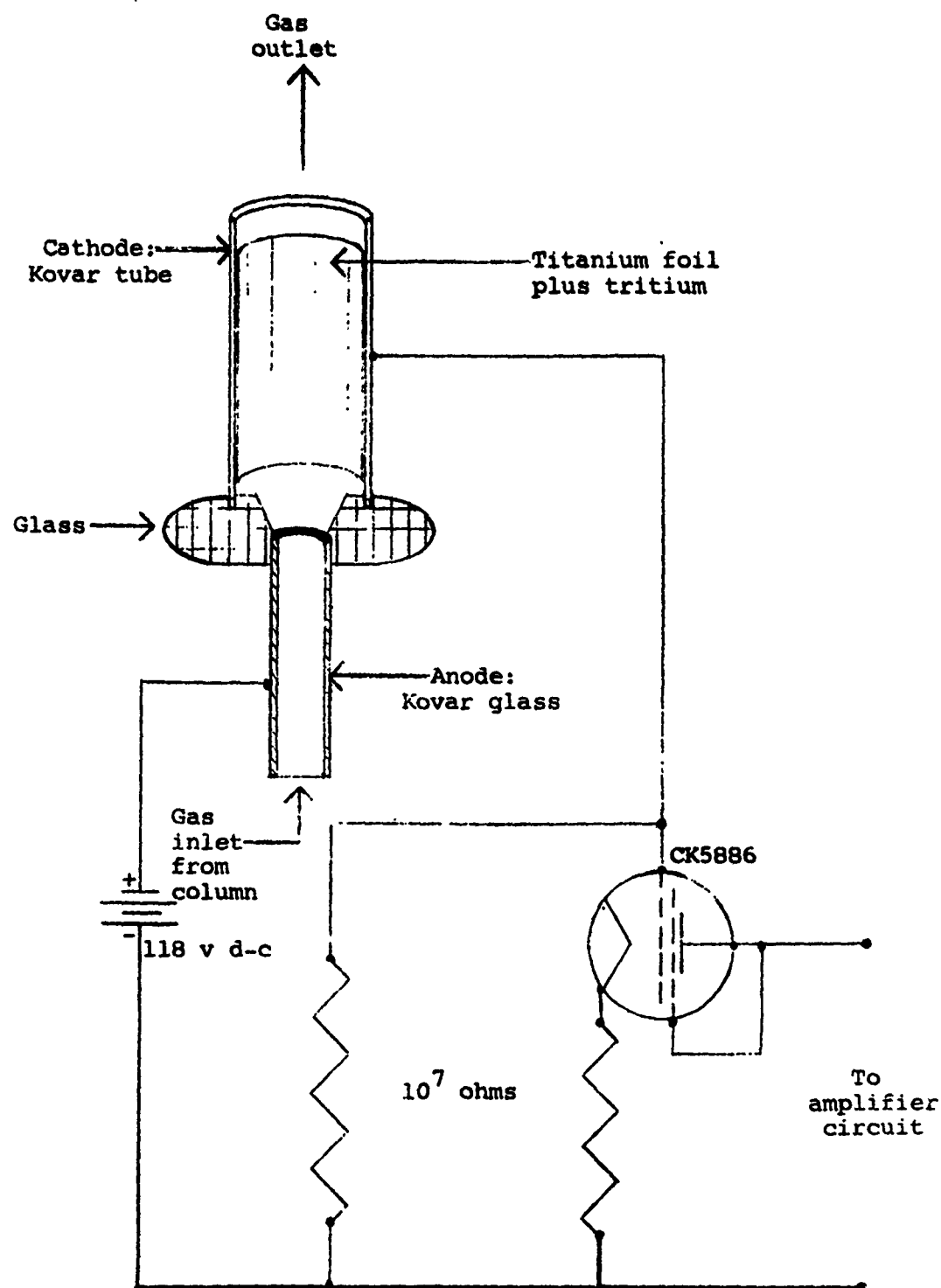


FIGURE 2 - Electron-Capture Detector and Circuit

Ordinarily, of course, gases are very poor conductors of electricity. Therefore, some means is necessary to introduce ions between the anode and the cathode of the detector to allow a current to flow between them. In this case, a foil of titanium metal that has been reacted with the radioactive hydrogen isotope, tritium, is the source of high-energy electrons (beta particles). These interact with carrier gas atoms to form positive ions and lower-energy slow electrons. Under the electrical potential provided by a battery, these electrons are collected at the positive electrode and the inlet tube. This causes a current to flow through the input resistor of an electrometer or d-c amplifier.

When any material that is capable of forming stable negative ions (anions) enters the detector, some of the electrons flowing toward the anode react to form such anions. Since the mobility of an anion is some 10^5 or 10^6 times less than that of the free electrons, the anions are carried away by the flowing carrier gas and react with positively charged gas molecules instead of being discharged at the anode. Hence the current flowing through the input resistor is greatly reduced, and an easily amplified and measurable signal is produced.

The processes in the detector are summarized in the following set of chemical equations.



In Reaction 1 tritium disintegrates radioactively to give a helium-3 positive ion and a beta particle with an energy of about 18,000 ev. By collisional interaction with the argon carrier gas, $n+1$ slow electrons are produced as in Reaction 2. The value of n is about 500 to 1000, since about 15 ev is required to ionize argon. The slow electrons either recombine with the positive argon ions or are collected by the anode. Otherwise, they react, as in Reaction 3, with some molecules that form stable negative ions, RX^- , and are thereby "captured." Hence the name "electron capture" detector.

Because of the nature of the processes in the electron-capture detector, such parameters as the applied voltage, type of carrier gas, temperature, pressure, gas flow rate, and type of electrometer affect the detection process and the instrument performance. Studies of these parameters are discussed in the following sections.

2.2.2 Selection of Carrier Gas and Cell Potential

The first detector model to be studied was the Wilkens Instrument and Research, Inc. electron-capture detector, catalog No. 01-060. This device has the concentric tube design described in the previous section. In various publications (ref. 1,2) the manufacturer suggests the use of nitrogen as a carrier gas at a flow rate of 20 to 40 cc/min. In our earlier work we found that argon and helium can also be used effectively.

The main effect of the cell potential is to increase the current through the cell. The steady current flowing when no material other than the carrier gas is entering the cell is called the "standing current." The percentage by which this current is reduced per unit concentration of vapor entering the cell is related to the sensitivity of the detector. Generally, the sensitivity is expressed in terms of the area under the curve of the recorder per unit mass of material. Over the useful range, where the response of the detector is linear or directly proportional to the sensitivity factor, the peak height is also proportional to the sensitivity factor. The linear range of response for most materials is from 10 to 30% decrease in the standing current.

In Figure 3 the effect of cell potential on standing current is plotted for the four carrier gases argon, helium, nitrogen, and air. The gases were "zero gases" from Matheson Co., Inc., East Rutherford, N.J., and were certified to contain less than 1 ppm hydrocarbons as measured by mass spectrometry.

The apparatus used was essentially as shown in Figure 1. The flow rate was 40 cc/min, the injector block temperature 140°C, the column temperature 75°C, the detector temperature 130°C, and the column 1/8-in. Pyrex glass 13 in. long coated with Carbowax 4000.

The electrometer used was a Burrell Corp. model K-7 with a 1-mv output for an input of 31.5×10^{-12} amp on the SS-1X sensitivity and attenuator settings. The recorder was a Barber-Coleman model 8300 recording potentiometer set for 1 mv full scale.

As seen from Figure 3, argon gave the highest standing current of the four gases studied. At a cell potential of about 134 v, argon gave a current of 2×10^{-8} amp, helium and nitrogen gave less than 1×10^{-8} amp, and air gave only about 0.2×10^{-8} amp.

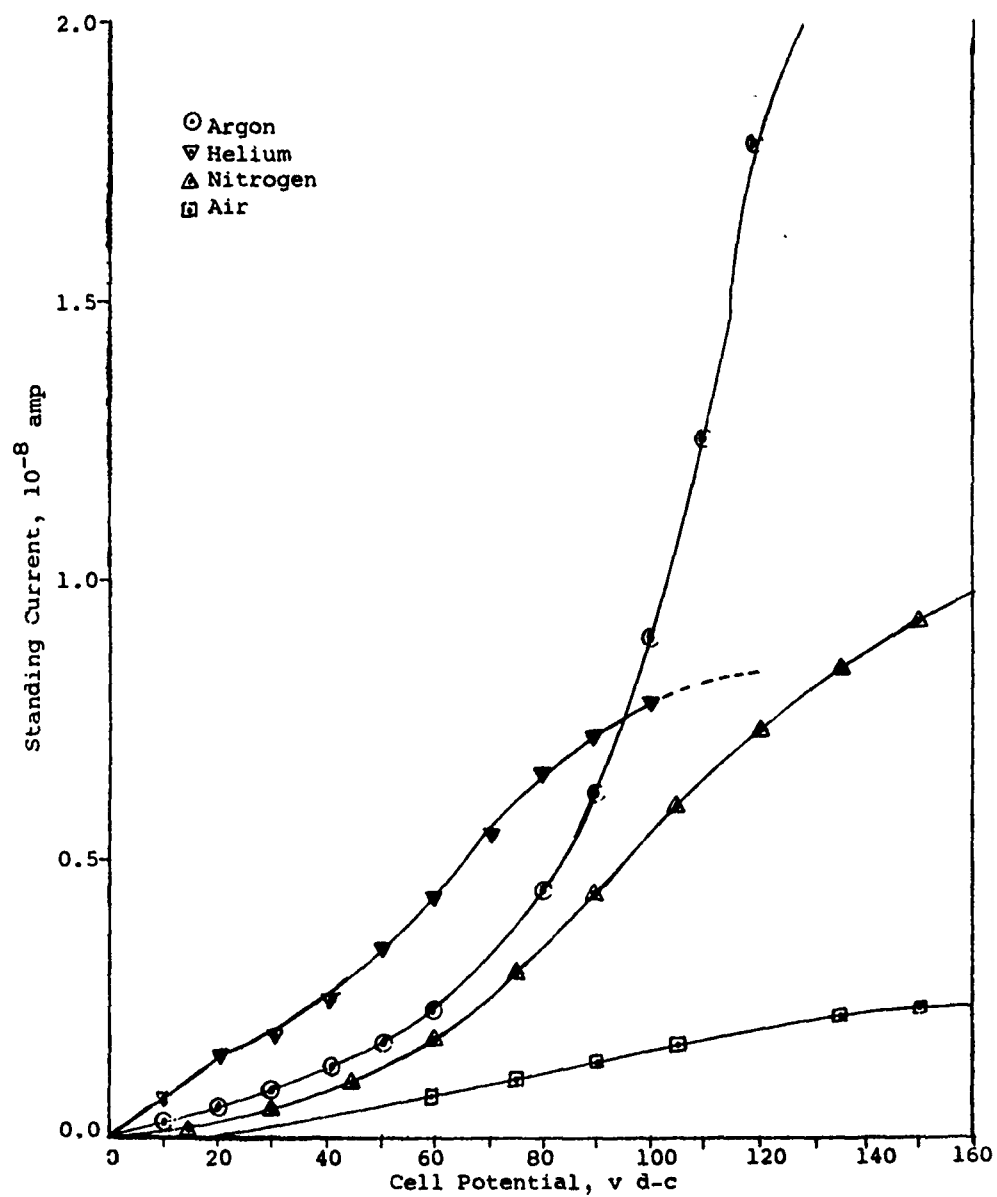


FIGURE 3 - Standing Current versus Cell Potential
for Various Carrier Gases

While the standing current was being studied, a study of the peak heights for different cell potentials and gases was also made. The test vapor was ethylene glycol dinitrate, EGDN, the substance found to emanate from many types of dynamite.

Samples of EGDN were obtained from the vapor space of a jar containing a commercial dynamite, DuPont Gelamite-II. A small stainless-steel syringe needle was inserted 3/8 in. into the jar through a silicone rubber septum. It was exposed to the EGDN vapors for exactly 10 sec (timed) and quickly transferred to the injection port. In this way, reproducible injections with a range of about $\pm 10\%$ were obtained. Estimates made from the previous work, the physical properties of EGDN (see Table IV), and the surface area of the needle indicated that samples containing about 20×10^{-9} g (or 20 ng) were injected by this technique.

The peak heights measured are shown in Figure 4. Argon gave the best response of the three gases run. Air was not tested because the low standing current makes it unsuitable.

Hence the optimum selections for carrier gas and cell potential for the cell chosen, were argon gas at 118 v d-c.

Another important point is the polarity of the cell potential, since basically the detector can operate with either polarity. In Figure 5 standing current versus cell potential is plotted for normal and reversed polarity. It is seen that reversing the polarity greatly reduced the standing current and therefore the sensitivity of the detector. Referring to Figure 2, the small inlet tube must be connected to the positive pole of the bias battery, as shown, for best response.

For comparison purposes, the cell current with and without EGDN at maximum concentration is plotted in Figure 6. It is evident from this figure that 118 v is the optimum voltage for maximum change in cell current with EGDN present.

The change in cell current with cell potential suggests that an a-c cell potential mode might be used for detection. To explore this possibility, an audiofrequency signal generator was placed in series with the battery between the battery and the 10^7 -ohm resistor shown in Figure 2. The a-c signal across the resistor was amplified, rectified, and fed to a recorder. No change in this signal was detected upon injection of EGDN. This indicates that the a-c component of the current in the resistor and cell circuit is very weakly dependent, if at all, on the flow of d-c current through the circuit.

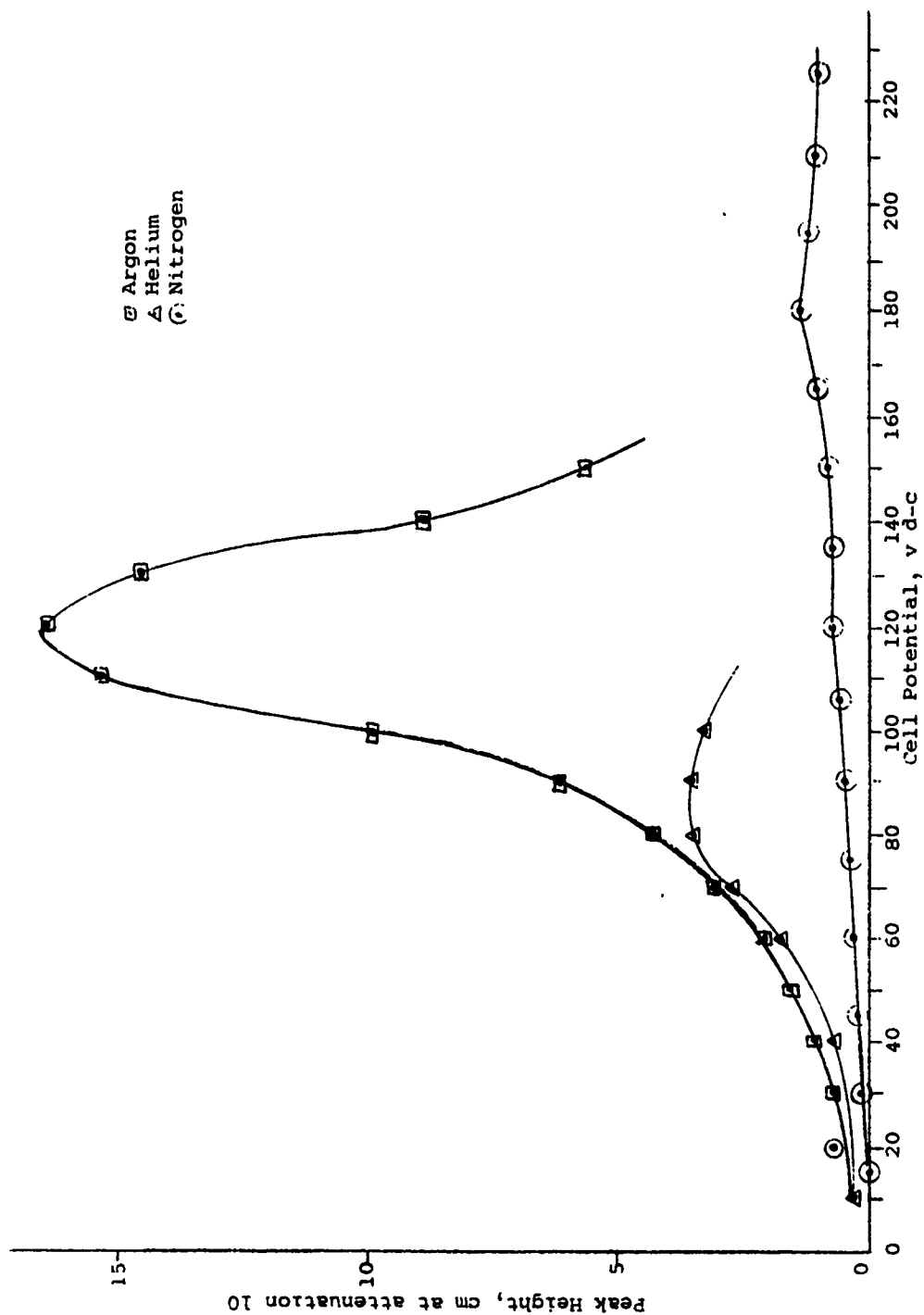


FIGURE 4 - Response versus Cell Potential for Various Carrier Gases

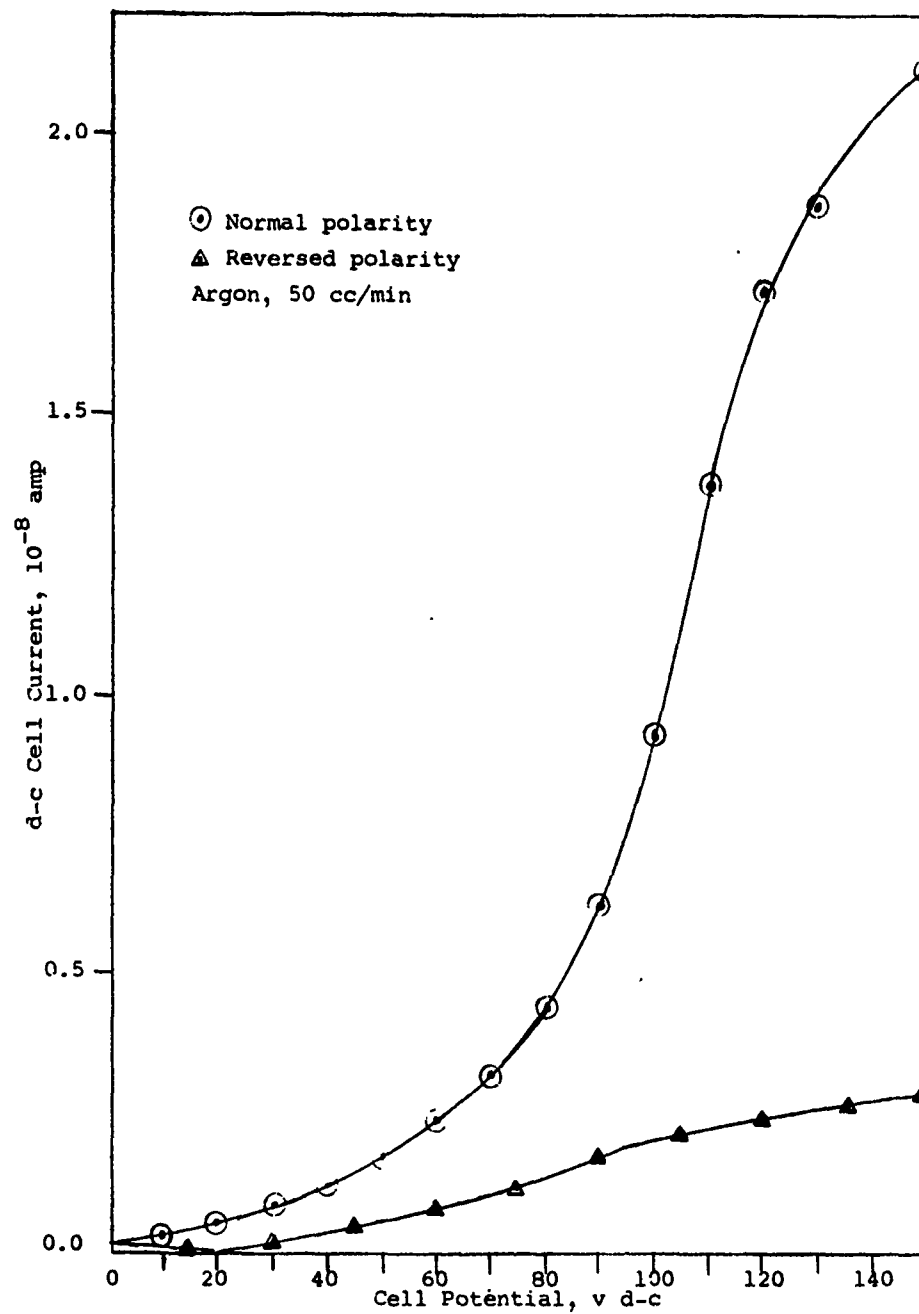


FIGURE 5 - Influence of Cell Polarity on Detector Response

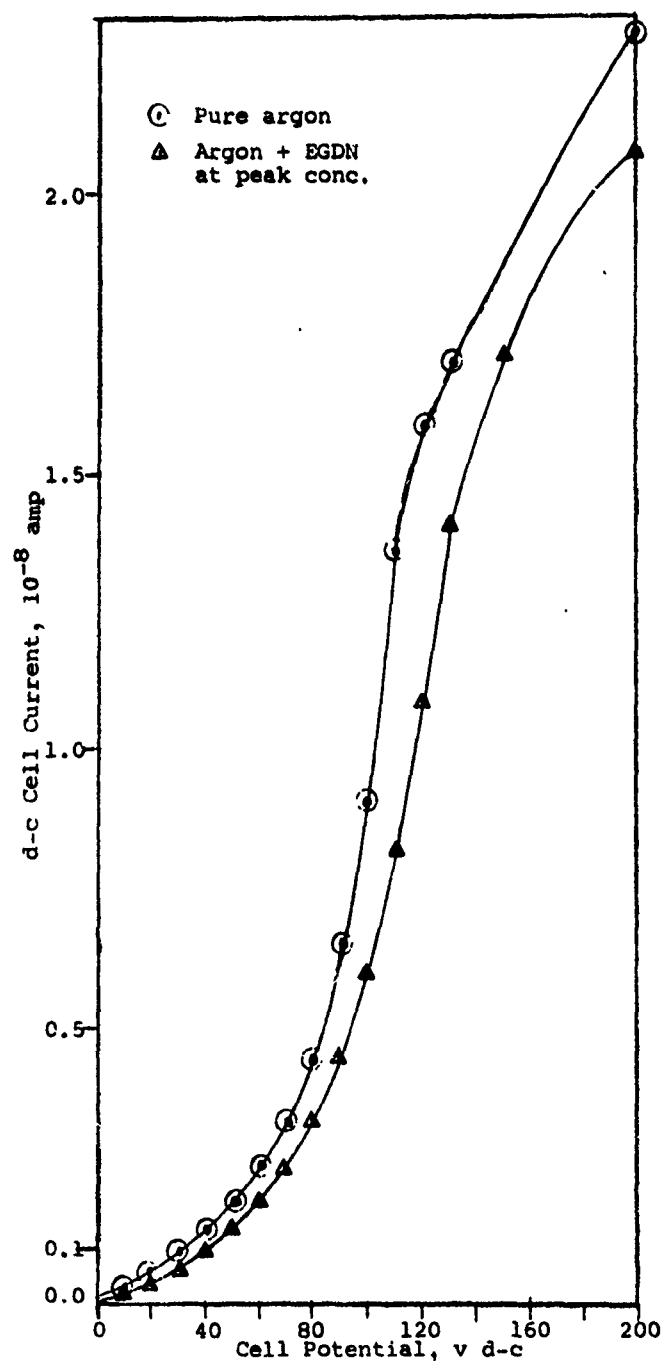


FIGURE 6 - Decrease in Standing Current caused by EGDN

In fact, the circuit tended to act like a series resistance capacitance circuit and the cell like a capacitor. This was indicated by the observation that as the frequency of the audio signal was increased, the a-c current increased.

Finally, the effects of flow rate on standing current, peak height, and retention time were determined for EGDN with argon carrier gas at a cell potential of 118 v d-c. The data are shown in Figure 7. Generally, above 20 cc/min the flow rate had little effect on the standing current or the peak height, but, of course, strongly affected the retention time. This effect is discussed in detail in Section 2.3.

2.2.3 Effect of Temperature

When the temperature of the electron-capture detector changes during an experiment, a large change in the base line of the standing current usually occurs. Other changes also take place.

In Figure 8 the effect of temperature on standing current is shown for the range 40 to 200°C. As is seen, the standing current increased by 5 to 6 times over this temperature interval. The inability to attain the same standing current upon heating and cooling is probably due to adsorption-desorption of some material on the electron-emitting surface.

Other important temperature-related factors are listed in Table I. These are: noise level, peak height, and peak width. The noise level decreased, the peak height increased, and the peak width decreased from 85 to 143°C. The change in peak height and width were probably due to less adsorption and to lingering of the vapor in the detector at higher temperature. This also resulted in less "tailing" (or unsymmetrical peaks) at higher temperatures -- a qualitative aspect of the peak shape not shown here. Because of thermal instability, the explosive vapors decompose at temperatures higher than 145 to 150°C.

On the basis of the above data, the desired detector temperature is 140°C with temperature controlled to within $\pm 0.1^\circ\text{C}$ to prevent oscillations of the standing current base line.

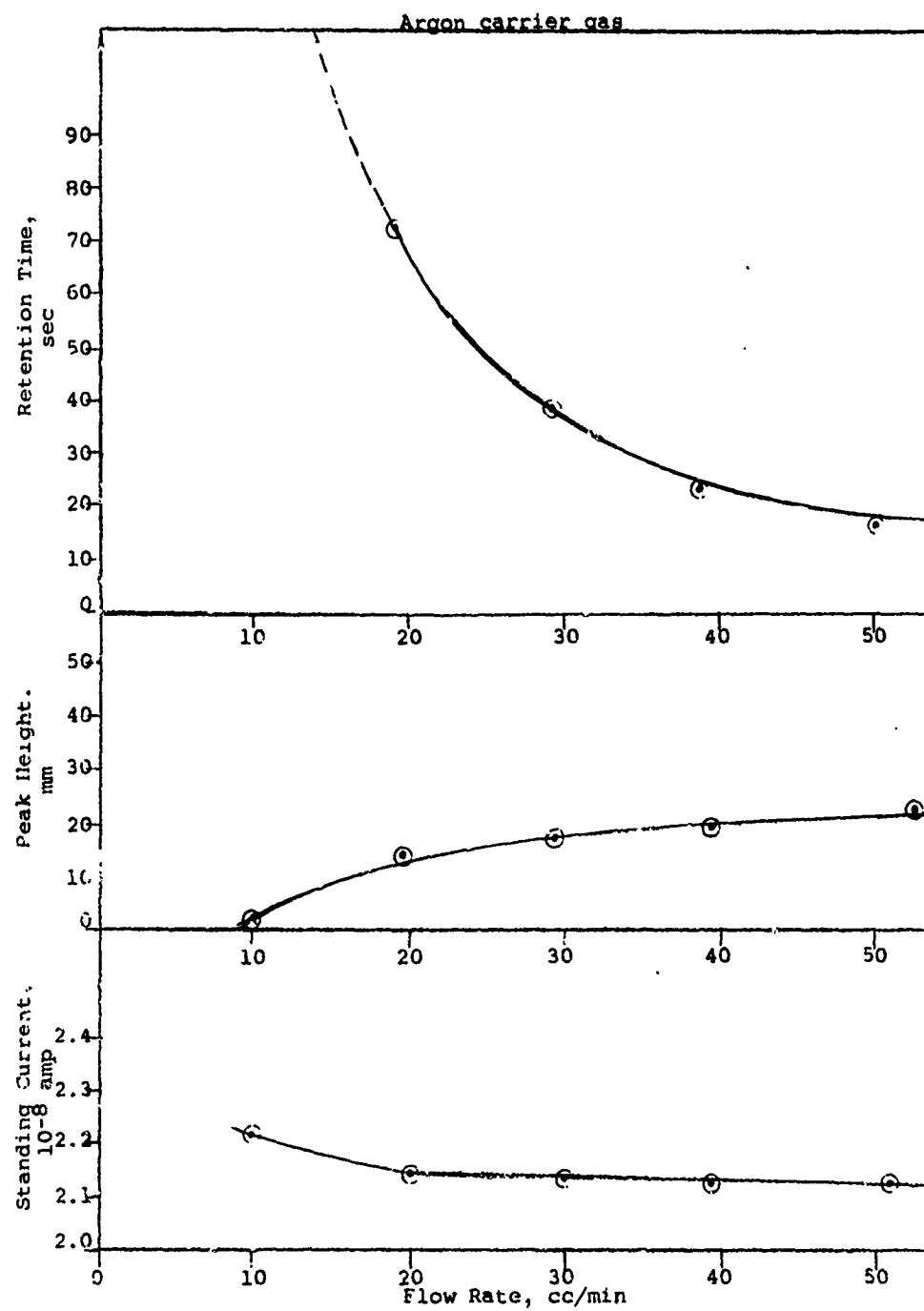


FIGURE 7 - Change in Signal Characteristics with Flow Rate

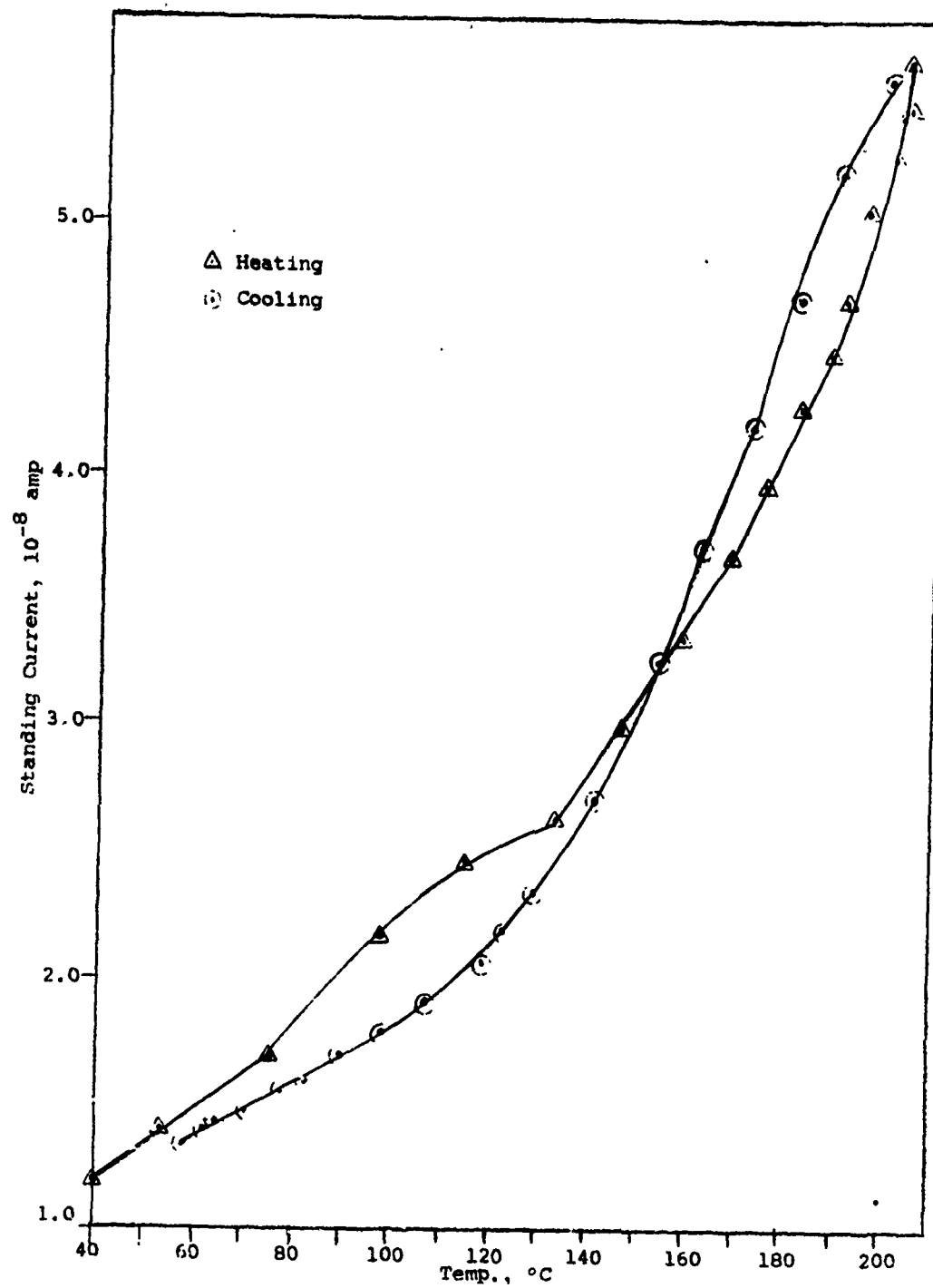


FIGURE 8 - Effect of Temperature on Detector Response

TABLE I - Effect of Temperature on Detector Parameters

Temp., °C	Standing Current, 10 ⁻⁸ amp	Noise (Peak to Peak), 10 ⁻¹⁰ amp	EGDN Peak Height, mm	EGDN Peak Half-Width, mm
85	1.60	1.38	80	4.8
110	1.95	1.26	109	2.0
143	2.75	0.94	113	0.8

Conditions:

Injection block 140°C.

Column 1/8-in. Teflon Tube, unpacked.

Column temp. 80°C.

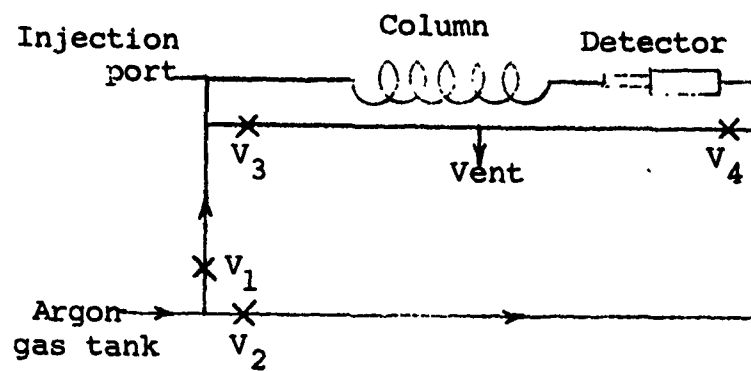
Flow 31.5 cc/min, argon.

Sample size ~20 ng EGDN from needle tip (see text).

2.2.4 Effect of Flow Reversal

In early studies with solutions of EGDN, dinitrotoluene, trinitrotoluene, and other vapors, we noted that occasionally a large flat peak appeared and the base line shifted. These effects were apparently due to some low-volatility material bleeding off the column slowly and reducing the standing current. Since the detector in the planned system need not function continuously but only when EGDN vapors are expected, it was decided to determine the effect of flow reversal. The purpose of reverse flow is to keep the detector free from any material that might bleed or enter from the column during the standby condition of the device. In the reverse mode, pure carrier gas flows first through the detector and then through the column.

A schematic of the valving arrangement used to study flow-reversal effect is shown in Figure 9. This is a simple modification of the system used in other studies of carrier gas. Instead of going directly from the argon gas tank to the injection port, the carrier gas entered a tee, where its path could be directed by simultaneous opening and closing of solenoid valves. Thus, when valve V₁ was open, the gas flowed to the column through the detector and on to the vent. In this mode, V₂ and V₃ were closed while V₁ and V₄ were open. By throwing a double-pole double-throw electric switch, the V₁ and V₄ closed and V₂ and V₃ opened. The carrier gas then entered the rear of the detector and passed through it and the column, etc. to the vent. A soap-bubble flowmeter was attached to the vent to measure the flow rates.



Valve System for Flow Reversal

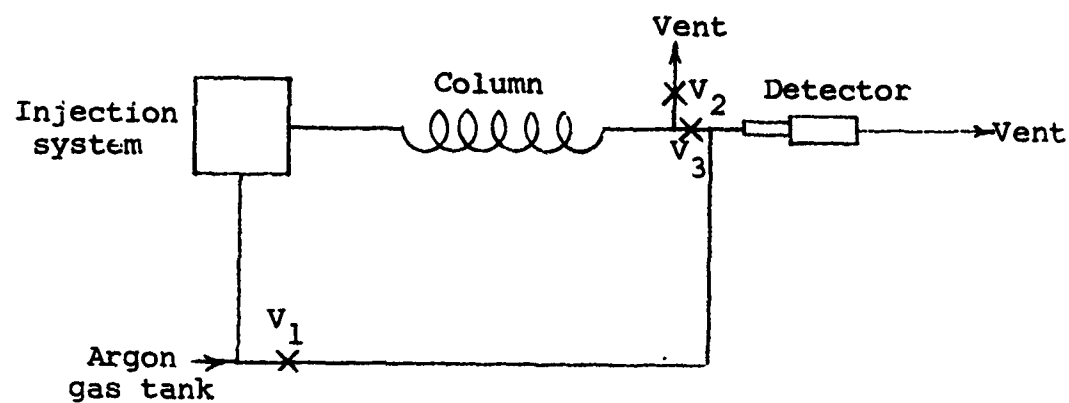


FIGURE 9 - Valving System Recommended for Maintaining a Clean Detector

The system was tested after it had run for about a day and the standing current had become constant. The flow rate in both directions was found to be the same -- 30 cc/min. The effect of flow reversal is illustrated in Figure 10, which shows standing current as a function of time. The standing current leveled out at 1.2×10^{-8} amp with forward flow. Upon reversing the flow from forward (through the column and then the detector) to reverse (through the detector and then the column), the current increased to 1.33×10^{-8} amp. This increase was rapid and required only about 11 sec to reach a steady value. However, upon returning to normal forward flow, the current returned to a steady value in about 3 min. The effect was not very large, being a change of about 10%, but the return to a steady value was relatively slow. Later work indicated that sufficient stability can be achieved as long as the backwash does not go through the whole forward flow system.

We have noted in other studies that changes in the flow rate from about 20 to 30 cc/min result in slight standing-current variations that disappear rapidly. Therefore, a system similar to that in Figure 9 is also feasible for maintaining a clean detector. Here the flow is always in the same direction through the detector. With valves V_1 and V_2 open and V_3 closed, the carrier gas passes through both the column and the detector but gas from the column is vented before it reaches the detector. When gas from the column with the detector is to be inspected valves V_1 and V_2 close and V_3 opens. Then the gas passes through the detector before it is vented. It should be possible to adjust the flow so that there is negligible change in flow rate through the detector during the switch from pure argon to sample gas.

2.2.5 Comparison of Commercial Detectors

Two other commercially available electron-capture detectors were compared with the model 680 Pestilyzer from Wilkens Instrument and Research, Inc.

The first model studied was a variable-space electron-capture detector from Loenco, Inc., Altadena, Calif. This was set up by using the Apiezon-N column used for the Wilkens detector. It was run with argon carrier gas and applied voltages from 10 to 130 v. It showed a maximum response of about half that of the Wilkens device at an applied voltage of 45 v. The trace showed much more trailing than the Wilkens model.

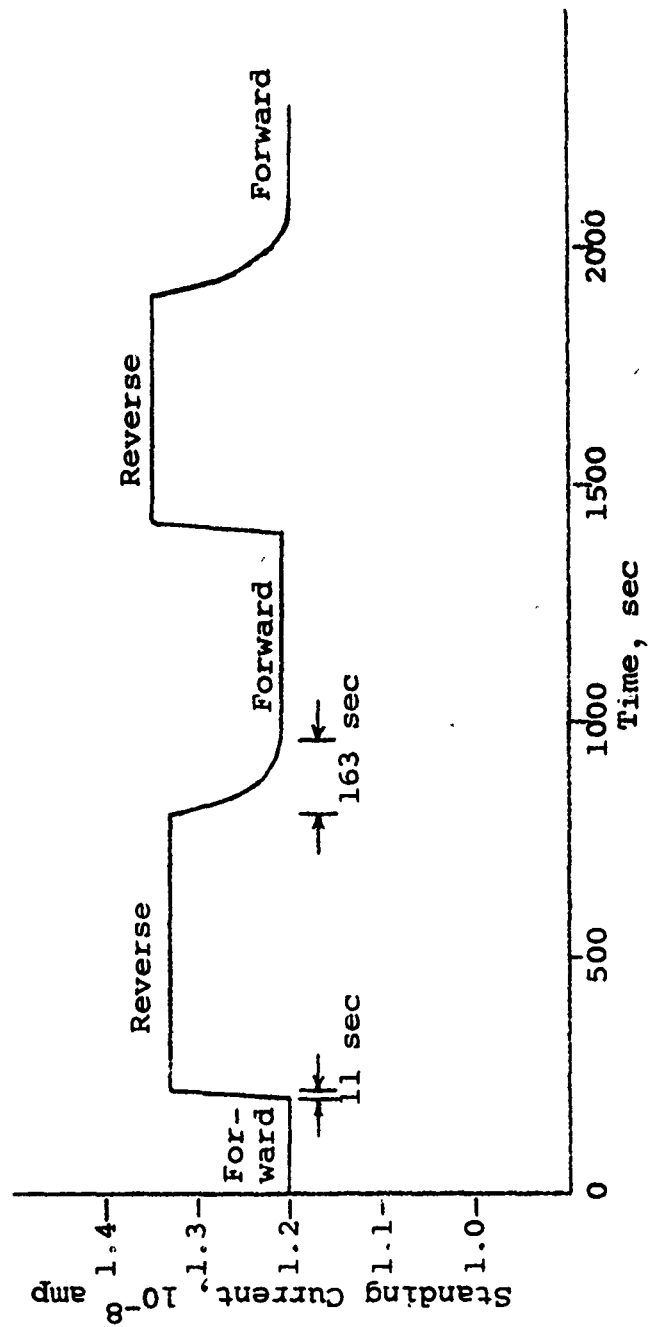


FIGURE 10 - Effect of Flow Reversal on Standing Current

The second detector studied was a variable-space electron-capture detector from the Jarrell-Ash Co., Waltham, Mass. It was operated at voltages from 10 to 130 v and under conditions similar to those of the above detectors. It showed a response similar to that of the Wilkens Model 680 Pestilyzer but much greater tailing and overlap of the EGDN and nitrobenzene peaks.

The tailing of the variable-space detectors is due to the internal geometry of the detector. It has a larger volume, having parallel electrodes instead of the concentric tube design of the Wilkens detector. Consequently, the vapors tend to linger in the detector much longer. Therefore, the Wilkens concentric design was selected over the Loenco or Jarrell-Ash parallel-plate design.

2.3 Selection of Column and Packing

The function of the partition column in an analytical gas chromatograph is generally to separate complex mixtures of organic substances. Since these mixtures often contain materials of very similar structure or properties, long periods of time or special techniques are required to achieve complete separation.

For the usual gas chromatographic work, the column is a 1/4-in. OD stainless-steel or copper tube about 10 ft long. It is packed with a powdered material about 60- to 80-mesh size. This powder may be ground firebrick, aluminum oxide, glass, or a wide variety of other inert materials. The powder is coated with a grease or viscous liquid up to about 15% by weight of the solid. This grease is called the "liquid phase" or the "stationary phase." In the work with EGDN, long tubes of catalytically active materials were found to be unsatisfactory, since EGDN decomposed. More inert materials, such as Teflon (DuPont polytetrafluoroethylene) and glass, were suitable.

The column is placed in a thermostat and attached to the injection block and the source of carrier gas. When a sample of dynamite vapors is injected into the hot injection block, the vapors pass over the coated particles. If the vapors are soluble in the liquid phase, they come to equilibrium with it, i.e., form a solution. As long as they remain in the liquid, they remain stationary and are not carried along the column in the carrier gas. This is why the liquid is called the stationary phase. As the carrier gas sweeps over the stationary phase, the vapors dissolved in it evaporate again into the fresh gas stream in a reversible dynamic equilibrium

and by continuous solution and evaporation migrate through the column. Finally, the vapors emerge at the exit of the column and enter the detector. Each vapor component migrates at a different rate and emerges at a different time, unless the components are very similar.

By this process, materials of different volatility are separated both in space and time. Highly volatile materials and permanent gases emerge very rapidly from most columns, while less volatile materials are retained for longer periods, depending on their volatility and specific interactions with the stationary phase.

2.3.1 Column Tubing and Packing Material

In most chromatographic work, a copper or stainless-steel tube is used as the container for the packing material of the separation column. Metal tubes were found to cause catalytic degradation or other chemical changes of the sample. Then more inert materials, such as glass or Teflon, were used, and these were the most likely candidates for the column. Other materials, such as quartz, polyethylene, and other plastics, are also possible, but Teflon is well known for its better stability and inertness over all other plastics.

Glass was found to adsorb EGDN too strongly, as shown by the following experiment. A 1/8-in. OD Pyrex glass tube 14 in. long was rinsed with high-purity ether and packed with 2.0 g of ether-rinsed glass beads 60-mesh size. This tube was installed in the chromatographic setup shown in Figure 1. This column was held at 80°C, and nitrogen gas was passed over it overnight at a flow of 20 cc/min. A small sample of EGDN was injected onto the column from the needle of a syringe. Several minutes later, a broad flat peak appeared on the strip-chart recorder. This indicated that the EGDN was being held on the glass surface because of interactions with various ions and radicals in the glass. If there were no such interactions, the EGDN would have emerged in a sharp, narrow peak a few seconds after the injection.

Figures 11 and 12 show the retention of EGDN and nitrobenzene versus reciprocal flow rate by an unpacked and a packed Teflon tube. Nitrobenzene is a common material likely to interfere with EGDN detection. Even the very inert Teflon has some retention for these vapors. Since both EGDN and nitrobenzene have nearly the same vapor pressure, they emerge at almost the same time.

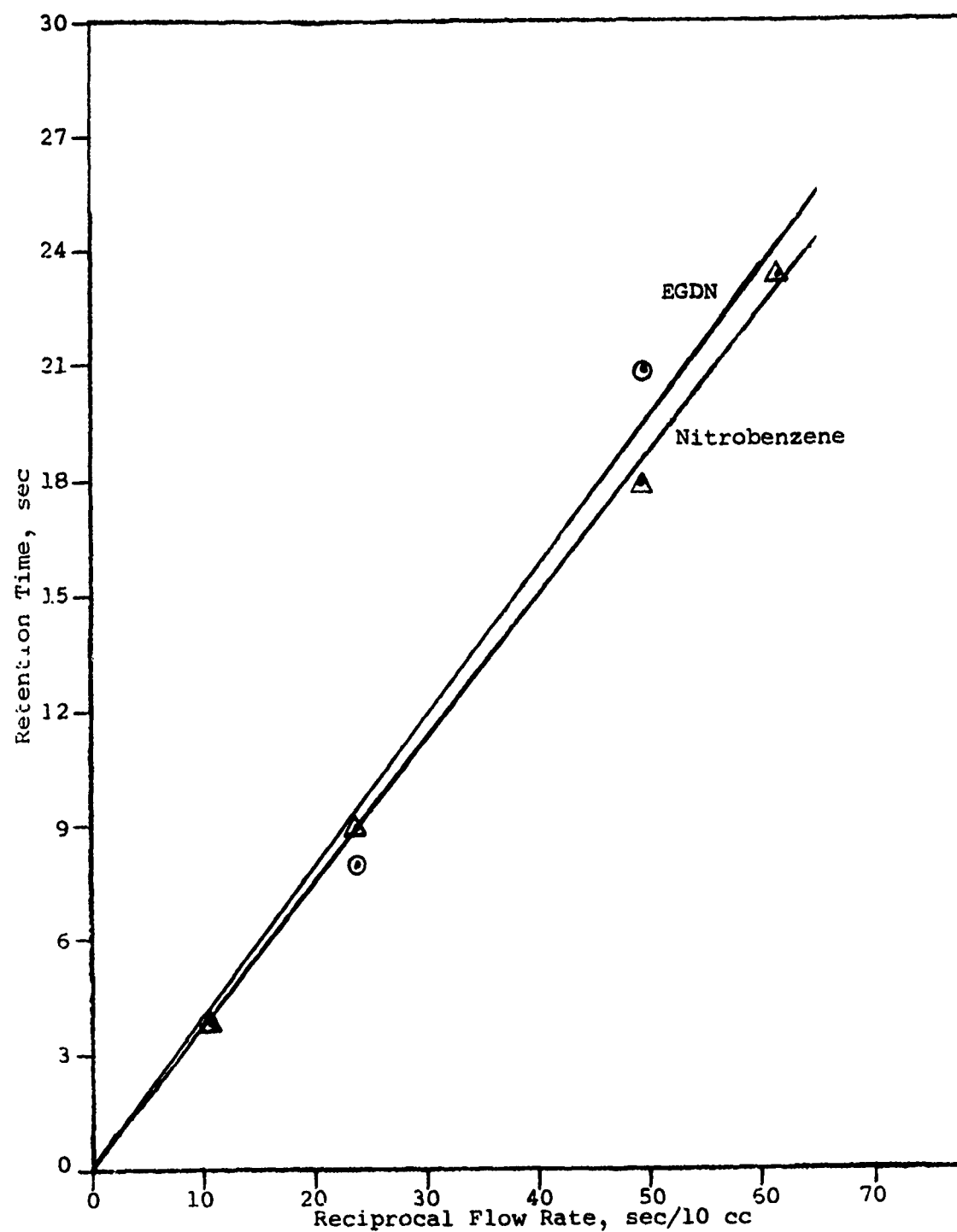


FIGURE 11 - Retention of EGDN and Nitrobenzene by an Unpacked Teflon Tube

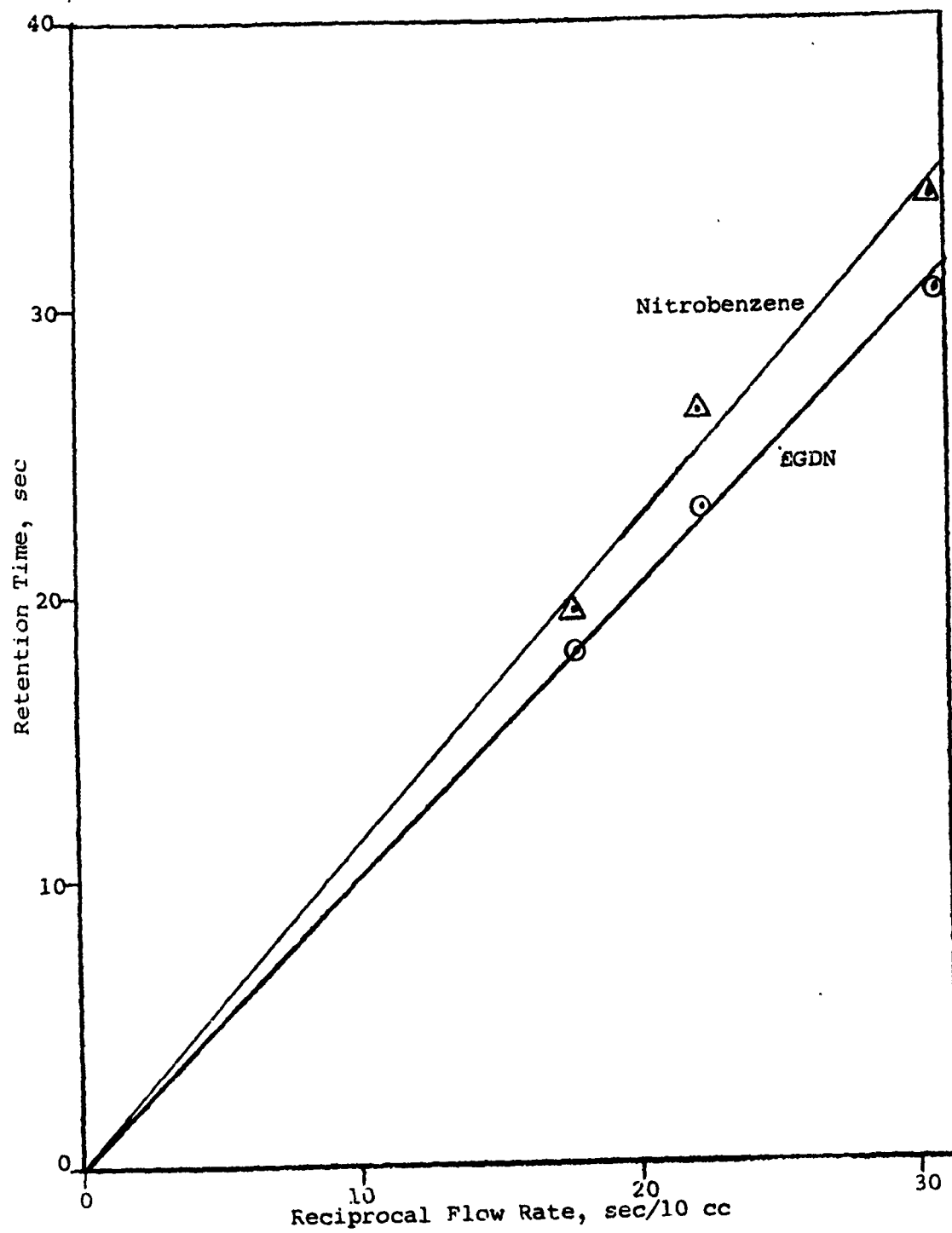


FIGURE 12 - Retention of EGDN and Nitrobenzene
by an Ether-Extracted Packed Teflon Tube

The packed column contained 1.0723 g of shredded Teflon held in place by a square plug of Teflon forced into either end. The injection block was at 126°C, the column at 82°C, and the detector at 131°C.

R_T , the retention time of the vapors, is plotted versus reciprocal flow rate, since R_T is inversely proportional to flow rate. A graph of R_T versus reciprocal flow rate should be a straight line passing through the origin, corresponding to zero time at infinite flow rate. As will be seen in Section 2.3.3, on column evaluations this relation appears to be true for most stationary phases.

The reciprocal flow rate data plotted on these and other graphs were corrected by the factor shown in the relation:

$$R_C = \frac{298}{T_C} \cdot R_M \quad (4)$$

where R_C is the corrected reciprocal flow rate; R_M is the measured reciprocal flow rate; T_C is the column temperature, °K; and 298 is the room temperature, °K. The reciprocal flow rate was measured by timing the motion of a soap film upward through a glass tube having a volume of 10 cc between two marks. An accurate stopwatch allowed measurement of this quantity to within a few hundredths of a second.

The slope of the retention time versus reciprocal flow rate curve is called the "retention volume" of the column for the vapor considered. This ratio as obtained from Figure 1.1 for the empty tube represents the "dead" volume (or empty space) within the injection block, the column, and the detector. The dead volume was found to be about 4 cc. The volume of the tube was about 2.0 cc, so that the injection block and the detector had a combined volume of 2 cc or less.

Thus Teflon appears to be a more useful column and column packing material than glass. Teflon has two important practical advantages over glass: it is flexible and it is not fragile. Therefore it is easy to install in a chromatograph and is not easily broken. All the studies on columns discussed below were made on ether-rinsed 1/8-in. OD Teflon tubing.

2.3.2 Column Preparation

Figure 13 is a diagram of an apparatus built for coating shredded Teflon packing material. A few grams of the packing is placed in the upper drying and coating chamber. A solution of about 10% by weight of the liquid phase in a suitable solvent is added to the shreds and stirred to attain a uniform coating. Suction then draws away the excess solution, and a small amount held up by the surface of the shreds remains. After being warmed to about 100°C in the lower chamber of the apparatus, dry filtered nitrogen gas is passed through the coated shreds. After about 15 to 30 min, the solvent is completely removed and the shreds are ready for use in a column.

Table II lists the coatings prepared in the above apparatus and the data on the columns made from them. The columns were 1/8-in. OD thin-walled Teflon tubing. They were rinsed with 50 ml of pure diethyl ether before they were filled. They were about 14 in. long, with the packed section about 10 in. long. Square plugs of solid Teflon forced into both ends held the packing in place. When a column was ready, it was placed in the chromatographic system and heated at 120°C overnight at a flow of 20 to 40 cc of carrier gas. This removed any small amount of remaining solvent and other volatile materials that might contaminate a detector.

TABLE II - Specially Prepared Coatings and Columns

<u>Stationary Phase</u>	<u>Avg Mol Wt, g/mole</u>	<u>Wt % of Coating</u>	<u>Packing, g</u>	<u>Liquid Phase, g</u>
Apiezon-N	1280	5.84	1.1868	0.0692
Apiezon-N + 8.94% carotene	1136	6.57	1.1450	0.0753
Apiezon-N + 8.9% biliverdin	1164	16.75	0.7204	0.1210
Carbowax 4000	2555	8.33	1.1714	0.0975

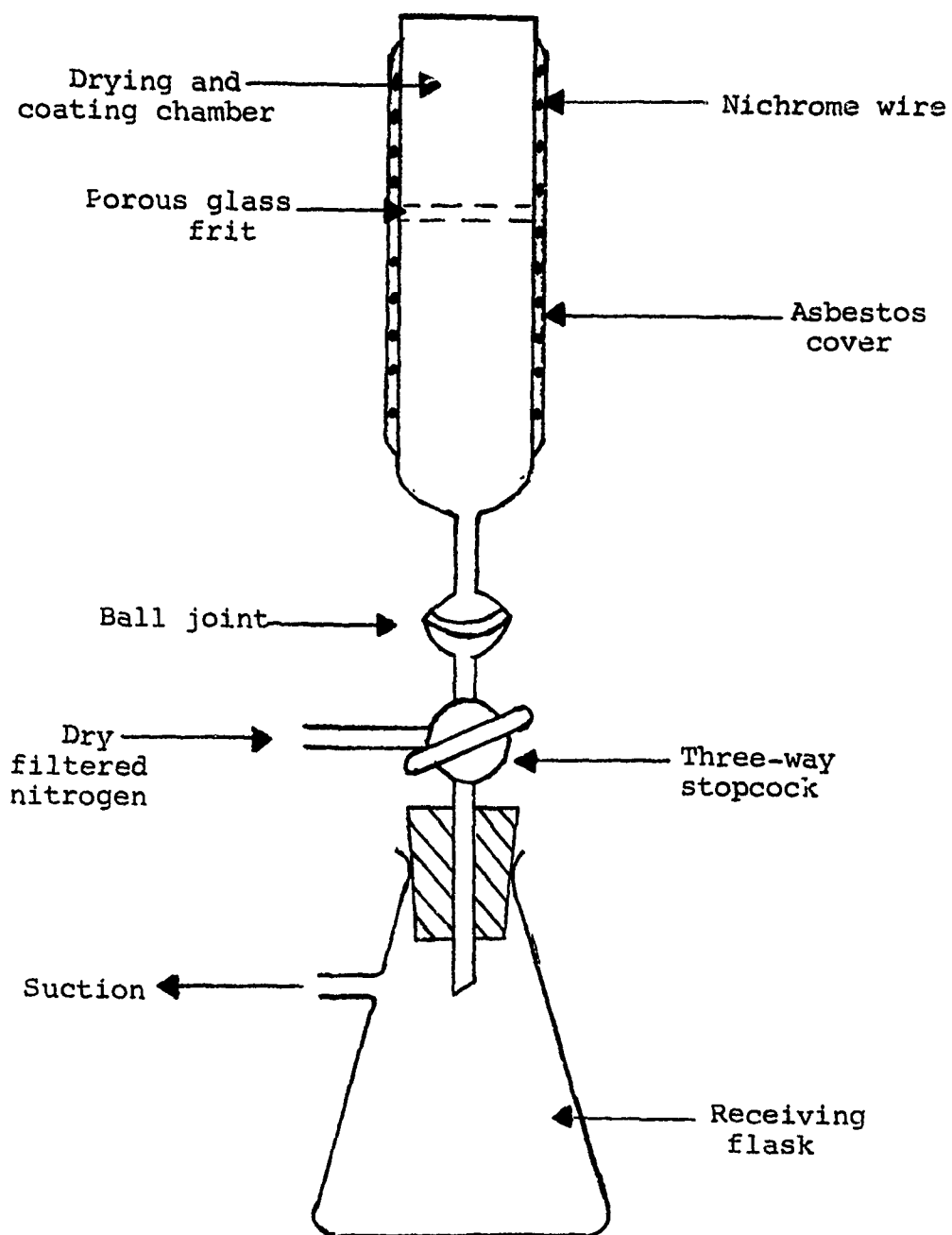


FIGURE 13 - Apparatus for Solution Coating of Gas Chromatographic Supports

Other coatings tested were obtained from the Varian-Aerograph Corp. in Walnut Creek, Calif. They are listed in Table III, together with data on amount and molecular weight of the coating. The molecular weights of Carbowax 4000 and Apiezon-N given in Table II and those of Silicone Ester-52 and Kel-F grease given in Table III were measured in our laboratory by a standard technique. The other molecular weights are based on structural formulas.

The rationale behind the choice of the coatings for the tests is given in Sections 2.3.5 and 2.3.6.

TABLE III - Commercially Prepared Column Packing

<u>Stationary Phase</u>	<u>Avg Mol Wt, g/mole</u>	<u>Wt % of Coating</u>	<u>Packing, g</u>	<u>Liquid Phase, g</u>
Squalene	422	10	1.713	0.1713
Silicone Ester-52	5675	10	1.304	0.1304
Dinonyl phthalate	419	10	1.402	0.1402
Kel-F grease	796	10	0.5687	0.05687

2.3.3 Column Parameters

The performance of columns used in gas chromatography depends on many parameters, including diameter, length, amount and distribution of liquid phase, mesh size of the solid support, chemical nature of the liquid phase, and temperature. In this study, however, we have a special problem not usually of utmost importance in analytical work in the laboratory. Namely, the separation and the detection processes must be accomplished as quickly and effectively as possible. This requirement immediately rules out long columns of large diameter, densely packed with large amounts of liquid phase.

A typical column is 1/4-in. OD by 10 ft long, contains about 75 g of packing and about 10 g of liquid phase, and has a dead volume of approximately 7 cc. Therefore about 14 sec is required for the carrier gas itself to pass through it. In other words, if the material to be detected passed

through the column without being absorbed on it, 14 sec would elapse before it was detected.

We found early in the program that such large columns hold the EGDN vapors much too long and the vapors decompose before they emerge for detection. On the other hand, short unpacked columns of small diameter with a coating on the walls only allowed very fast detection of EGDN vapors but insufficient separation of the EGDN signals from oxygen signal produced by air. Therefore we decided to use 1/8-in.-OD columns about 14 in. long packed with Teflon shreds coated with the various types listed in Tables II and III.

2.3.4 Physical Properties of EGDN and Nitrobenzene

In an investigation of possible interferences from normal atmospheric contaminants in the detection of EGDN, we found that nitrobenzene had almost exactly the same retention characteristics as EGDN. Nitrobenzene is a common ingredient in shoe polish and other waxes as a softening agent and solvent.

The most important property of a material with regard to passage through a chromatographic column is its vapor pressure. Generally, the higher the vapor pressure, the more quickly a substance passes through the column. This is so because at a high vapor pressure more of the substance is in the gaseous and moving phase than in the liquid or stationary phase.

Figure 14 is a plot of the logarithm of vapor pressure versus the reciprocal of absolute temperature for EGDN and nitrobenzene. The data were taken from the Handbook of Physics and Chemistry, 44th edition, 1962.

Other properties of these materials, given in Table IV, are also taken from the Handbook. Most of the entries are self-explanatory. The boiling point of EGDN is in parentheses because it was obtained by extrapolation to 760 mm Hg.

ΔH_v , the enthalpy (or heat) of vaporization is also obtained from the plot in Figure 14 by using the thermodynamic equation:

$$\log_{10} p^\circ = - \frac{\Delta H_v}{2.3R} \cdot \frac{1}{T} + B \quad (5)$$

ΔH_v is related to the slope of the curve, as can be seen in the equation.

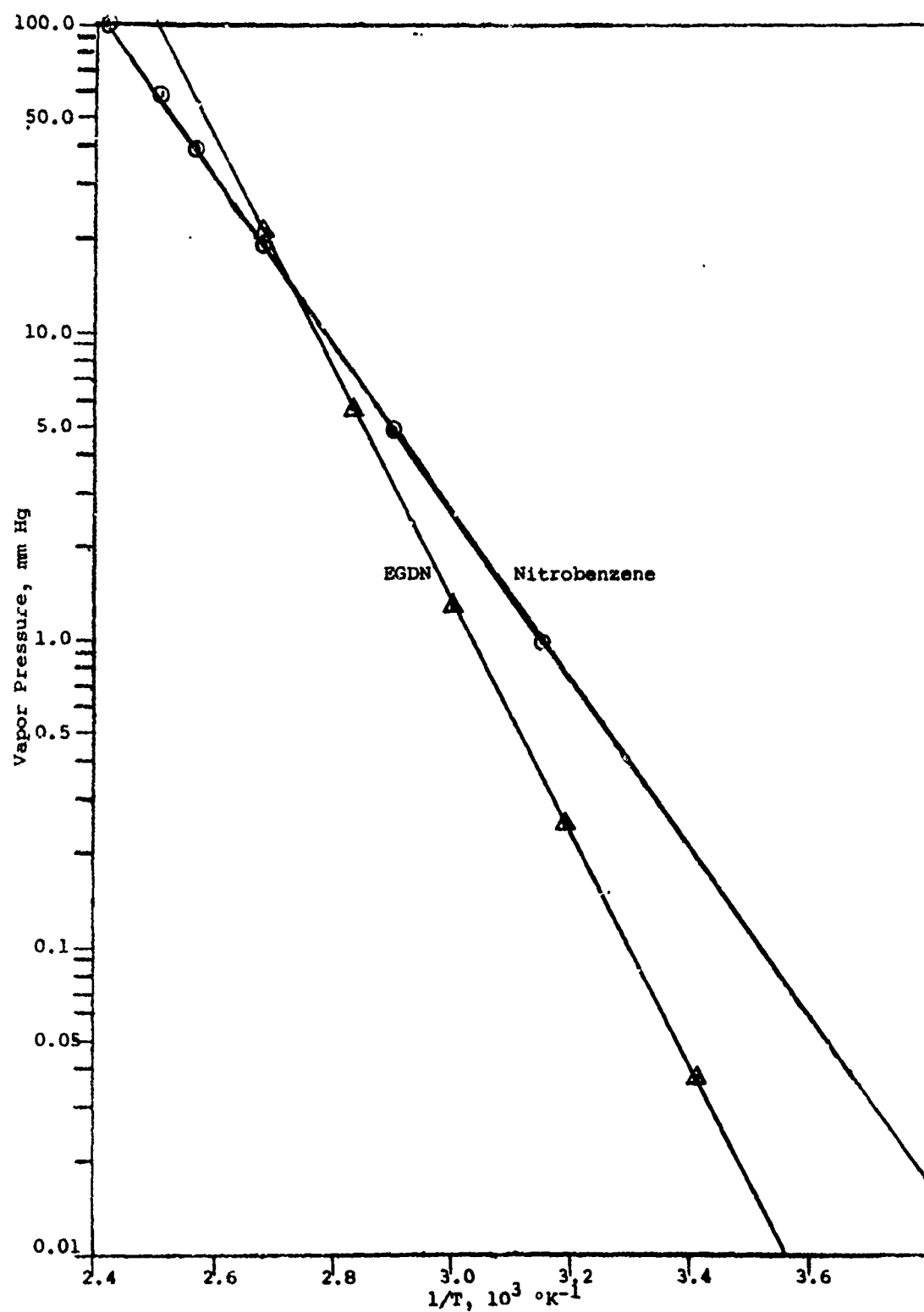


FIGURE 14 - Log Vapor Pressure versus Reciprocal Temperature for EGDN and Nitrobenzene

TABLE IV - Physical Properties of EGDN and Nitrobenzene

Property	EGDN	Nitrobenzene
Formula	$C_2H_4N_2O_6$	$C_6H_5NO_2$
Structure	$ \begin{array}{c} H \quad H \\ \quad \\ H-C-C-H \\ \quad \\ O \quad O \\ \quad \\ O-N \quad N-O \\ \quad \\ O \quad O \end{array} $	$ \begin{array}{c} O \quad O \\ \diagdown \quad / \\ N \\ \\ C \\ / \quad \backslash \\ HC \quad CH \\ \quad \\ HC \quad CH \\ \backslash \quad / \\ C \end{array} $
Molecular weight, g/mole	152.07	123.11
Density at 20°C, g/cc	1.483	1.19867
Melting point, °C	-20	5.7
Boiling point, °C	(169)	210.9
ΔH_v , enthalpy of vaporization, cal/mole	17,300	15,720
ΔS_v , entropy of vaporization, cal/mole-°K	39.15	32.50

ΔS_v is obtained from ΔH_v and the temperature at the boiling point based on the extrapolated EGDN data. The relation is:

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad (6)$$

where T_b is the boiling point, °K.

The values of ΔH_v and ΔS_v for EGDN and nitrobenzene are considerably larger than for most organic compounds of similar molecular weight. They indicate a high degree of intermolecular association in the liquid state.

Large entropy and enthalpy changes upon vaporization almost always point to a molecular structure showing high dipole

moment or hydrogen bonding. This means the molecules somehow have a partial separation of the average centers of positive and negative charges. The positive and negative poles (hence "dipole") of the molecules influence each other much like a bunch of magnets might line up with north and south poles alternating from molecule to molecule. This results in short-range structure in the liquid phase; this is not possible in completely symmetrical molecules like simple hydrocarbons. Since entropy is a measure of disorder in a chemical system, a large increase in entropy as liquid EGDN changes to gaseous EGDN means that EGDN is more ordered when in the liquid phase.

These considerations alone helped suggest some types of columns. It was expected that coatings having highly polar groups would show greater retention times for these molecules than nonpolar coatings. This was borne out in the studies of the thermodynamics of separation processes, which are discussed after the presentation of data on the columns listed in Tables II and III.

2.3.5 Apiezon-N and Doped Apiezon-N Columns

Column packings divide themselves naturally into two broad classes in their molecular interactions: polar and nonpolar. Apiezon-N grease represents possibly the most nonpolar weakly interacting material commonly available. All other nonparaffinic coatings represent various degrees of polarity with weak to strong molecular interactions.

In Figure 15 and 16 the actual traces obtained from the strip-chart recorder are reproduced. The column was Apiezon-N on shredded Teflon. Note the essentially complete separation of EGDN and nitrobenzene.

In Figure 15 the flow rate was 18.0 cc/sec. The first peak to emerge was EGDN, with its maximum at about 3 min. The next peak at about 8 min, was nitrobenzene. In Figure 15B and C the flow rates were 42.8 cc/sec and 32.4 cc/sec, respectively. In each, the first peak was EGDN, the second nitrobenzene. Changing flow rate never interchanges the order in which the peaks emerge. Flow rate controls only the total time required to elute any substance from a column.

The other conditions for each column were as follows:

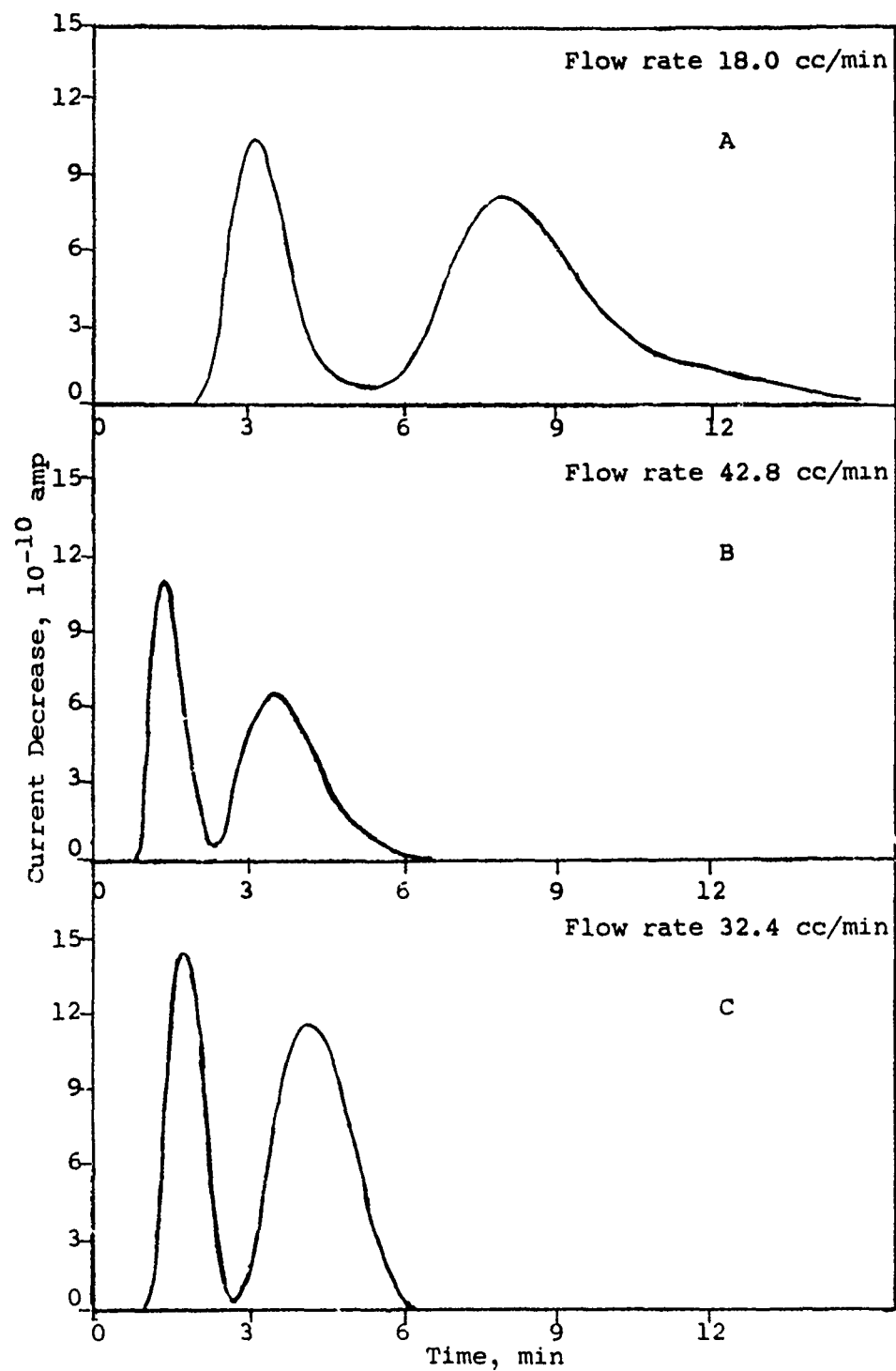


FIGURE 15 - Chromatograms of Mixtures of EGDN and Nitrobenzene Separated on Apiezon-N at 82°C and at Flow Rates Indicated

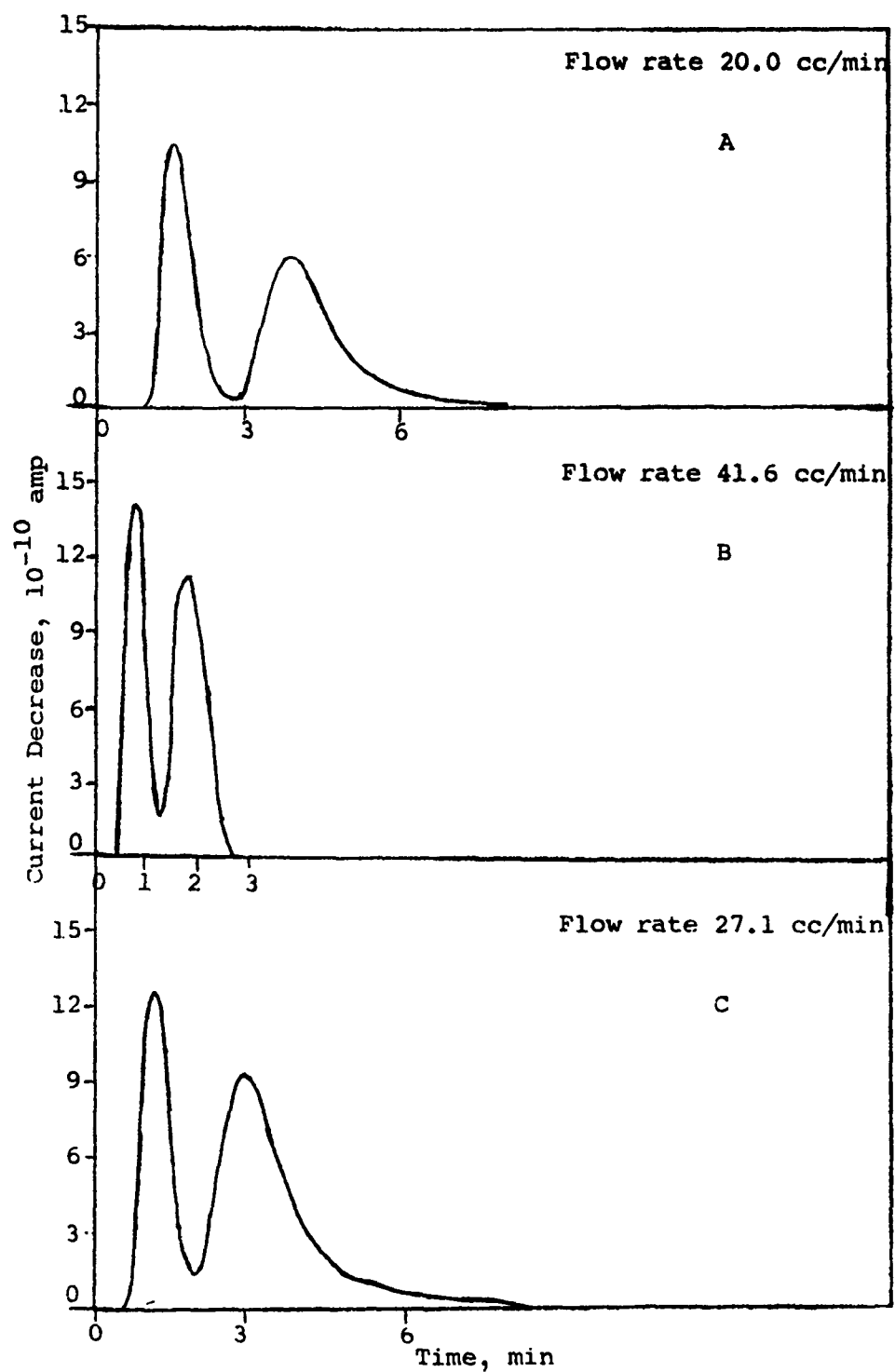


FIGURE 16 - Chromatograms of Mixtures of EGDN and Nitrobenzene Separated on Apiezon-N at 96°C and at Flow Rates Indicated

Carrier gas:	Argon, 99.96% pure
Injection block temp.:	135°C
Detector temp.:	130°C
Detector:	Aerograph Pestilyzer model No. 01-060 (electron-capture type)
Electrometer:	Burrell Corp. model K7
Sensitivity:	10x
Attenuator:	1A
Recorder:	Barber-Coleman Co.
Range:	1 mv full scale
Chart speed:	1/3 ipm

Figures 15 and 16 can also be compared with respect to the effect of temperature. Comparison of Figure 15A with Figure 16A shows that raising the temperature from 82 to 96°C reduced the retention time on the Apiezon-N coating considerably. Similar effects occurred at the other flow rates.

Another characteristic of chromatographic curves is their shape. An ideal trace is narrow (i.e., has a width at half-height to height ratio of about 1:10) and is symmetrical around a vertical line through the time of maximum response. As can be seen in Figures 15 and 16, EGDN, the first and higher peak, fulfills these requirements almost perfectly, while nitrobenzene, the second peak, although not badly distorted, is less ideal. At the slower flow rates tailing (or peak asymmetry) is most noticeable for nitrobenzene.

For the purpose of summarizing and presenting the data on the various columns studied, graphs of retention time versus reciprocal flow rate were prepared from the raw data and are represented in Figures 17 through 22.

In Figures 17 and 18 the retention times for EGDN and nitrobenzene, respectively, are plotted versus reciprocal flow rate. Theoretically, the observed points at any given temperature should lie on a straight line passing through the point 0.0, corresponding to zero retention time at infinite flow rate. As is seen in these and other figures, this behavior was neatly borne out in most cases.

Each graph contains a small table in which the retention volume of EGDN or nitrobenzene on the coating being examined is presented. This retention volume, V_R , is, in reality, the volume of gas that passed through the column while the substance was eluted.

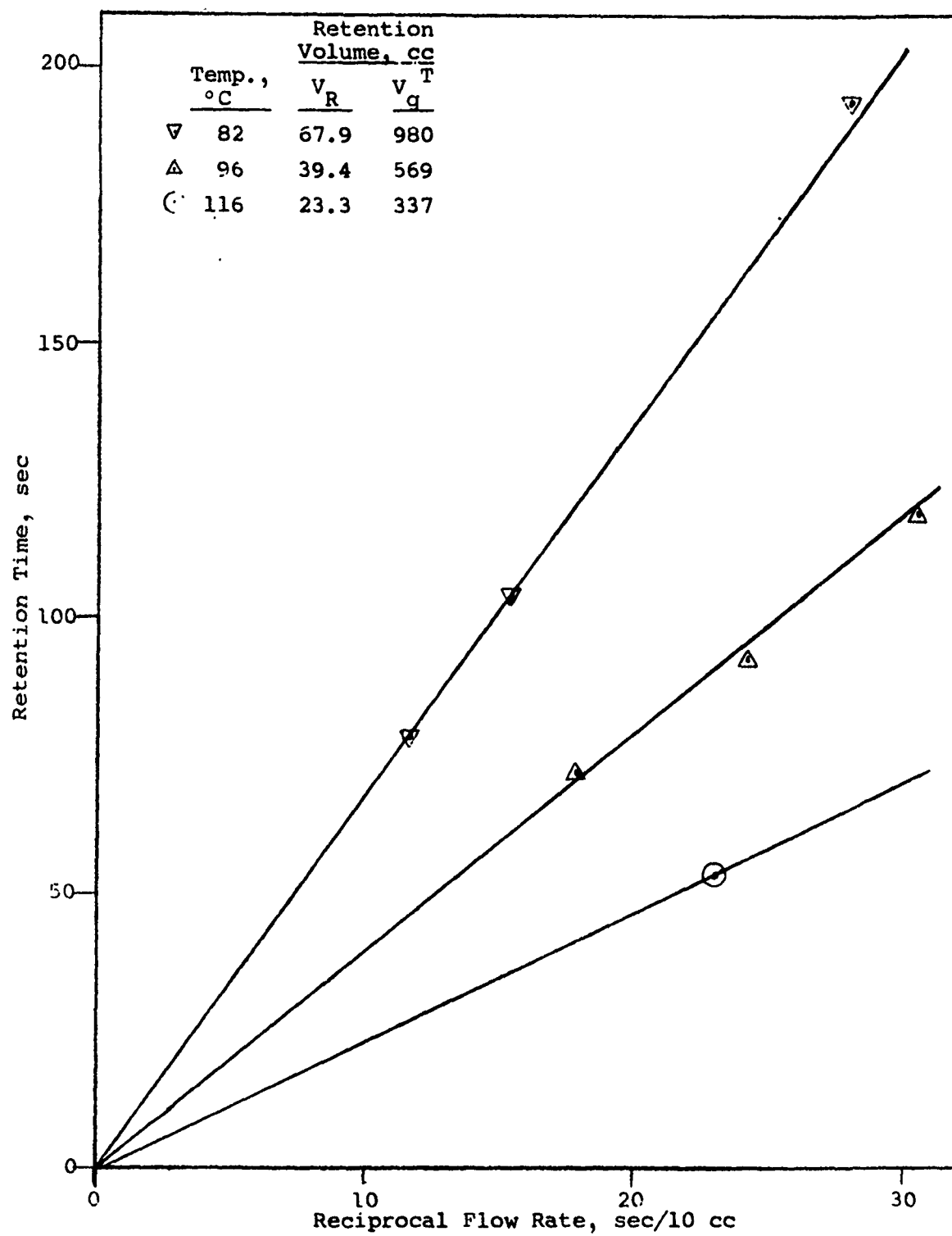


FIGURE 17 - Retention of EGDN by Apiezon-N Grease

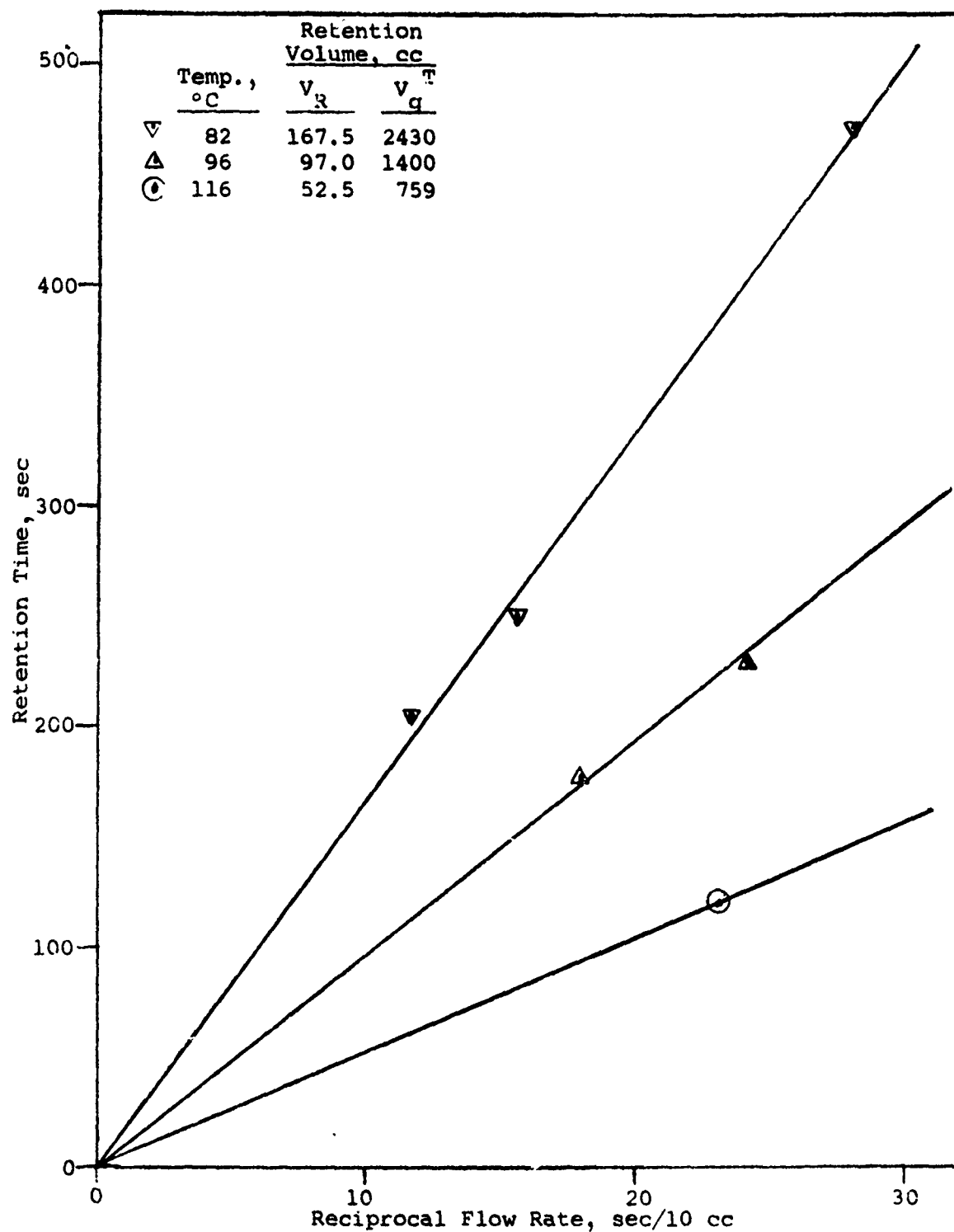


FIGURE 18 - Retention of Nitrobenzene by Apiezon-N Grease

V_R was obtained from the ratio of retention time and reciprocal flow rate, i.e., the slopes of the straight lines. The errors in measuring flow rate and retention time were ± 1 to $\pm 5\%$, or about the size of the circles around the plotted points.

Since EGDN and nitrobenzene are electron acceptors but are different in structure, we decided to determine whether adding electron donors to the coating influences the separation. In Figures 19 through 22 the retention times of EGDN and nitrobenzene are plotted for two doped Apiezon-N columns. It was hoped that the doping agent would form a molecular or charge-transfer complex with the EGDN or with the nitrobenzene especially. Much spectroscopic information in the recent literature (see, for example, Andrews and Keefer, ref. 3) indicates the formation of 1:1 molecular complexes between electron donor molecules and electron acceptor molecules. For doping, the donors must be nonvolatile, so that they do not bleed from the column. The electron donor materials chosen were carotene and biliverdin.

Two other electron donor substances, pyrene and chrysene, were also tried as doping agents, but their vapor pressures were too high. Also, they adversely affected the detector sensitivity by lowering the standing current.

Further discussion of the effects of doping is presented in Section 2.3.8 on thermodynamics of separation processes.

2.3.6 Polar Columns

In an effort to find a coating material more effective than Apiezon-N in separating EGDN and nitrobenzene, five other coating materials were studied. These included the very polar Carbowax 4000, which is a polyglycol material consisting of a carbon chain with a hydroxyl (OH) group on each carbon atom and some ether linkages.

Comparison of Figure 23 for Carbowax with Figures 17 and 18 for Apiezon-N shows that the order in which the EGDN and nitrobenzene emerged from the column was reversed. On Apiezon-N, EGDN appeared first, while on Carbowax, nitrobenzene appeared first. This is undesirable, since its peak would obscure the EGDN peak. Also, the Apiezon-N coating has better separating power and is therefore preferable.

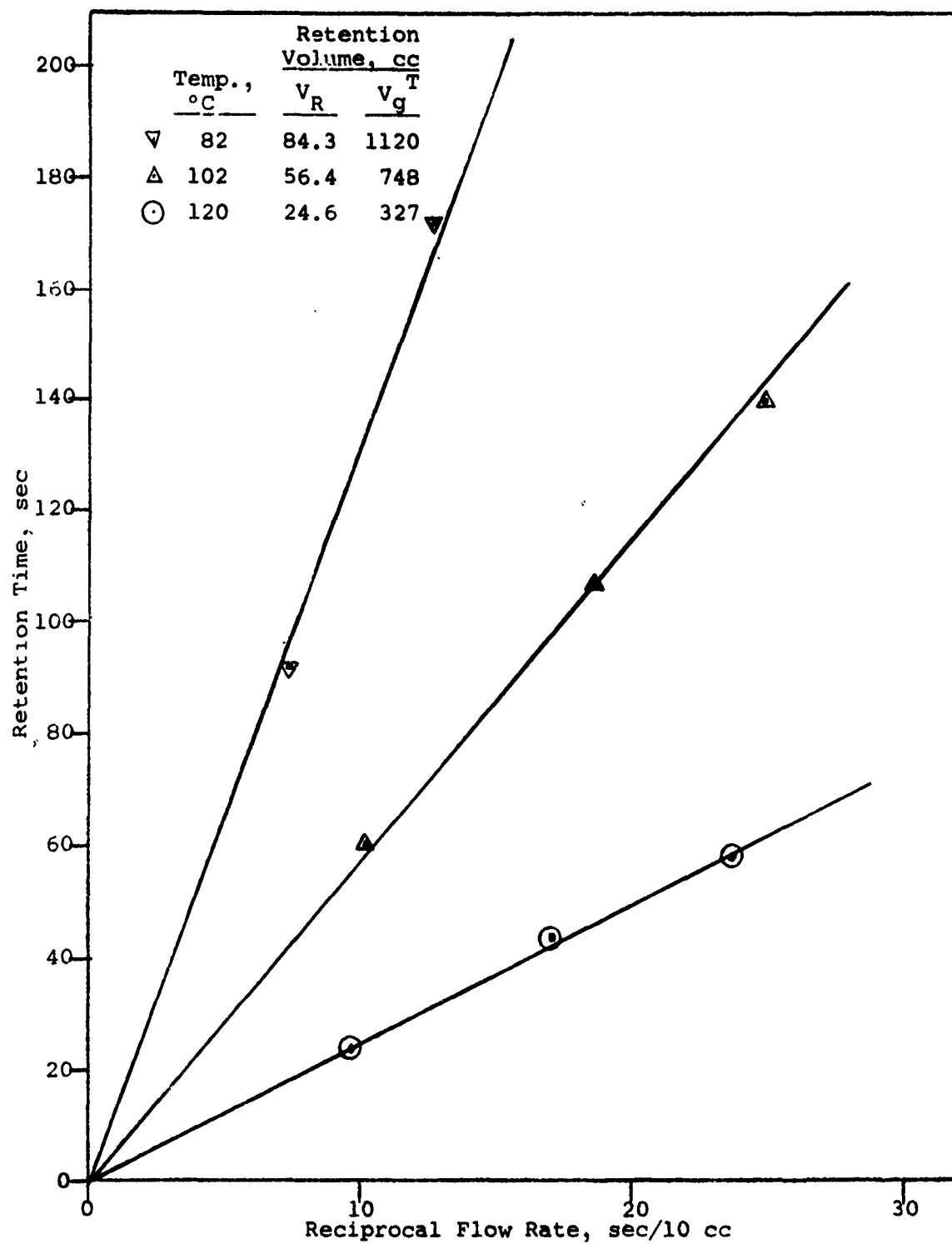


FIGURE 19 - Retention of EGDN by Carotene-Doped Apiezon-N Grease

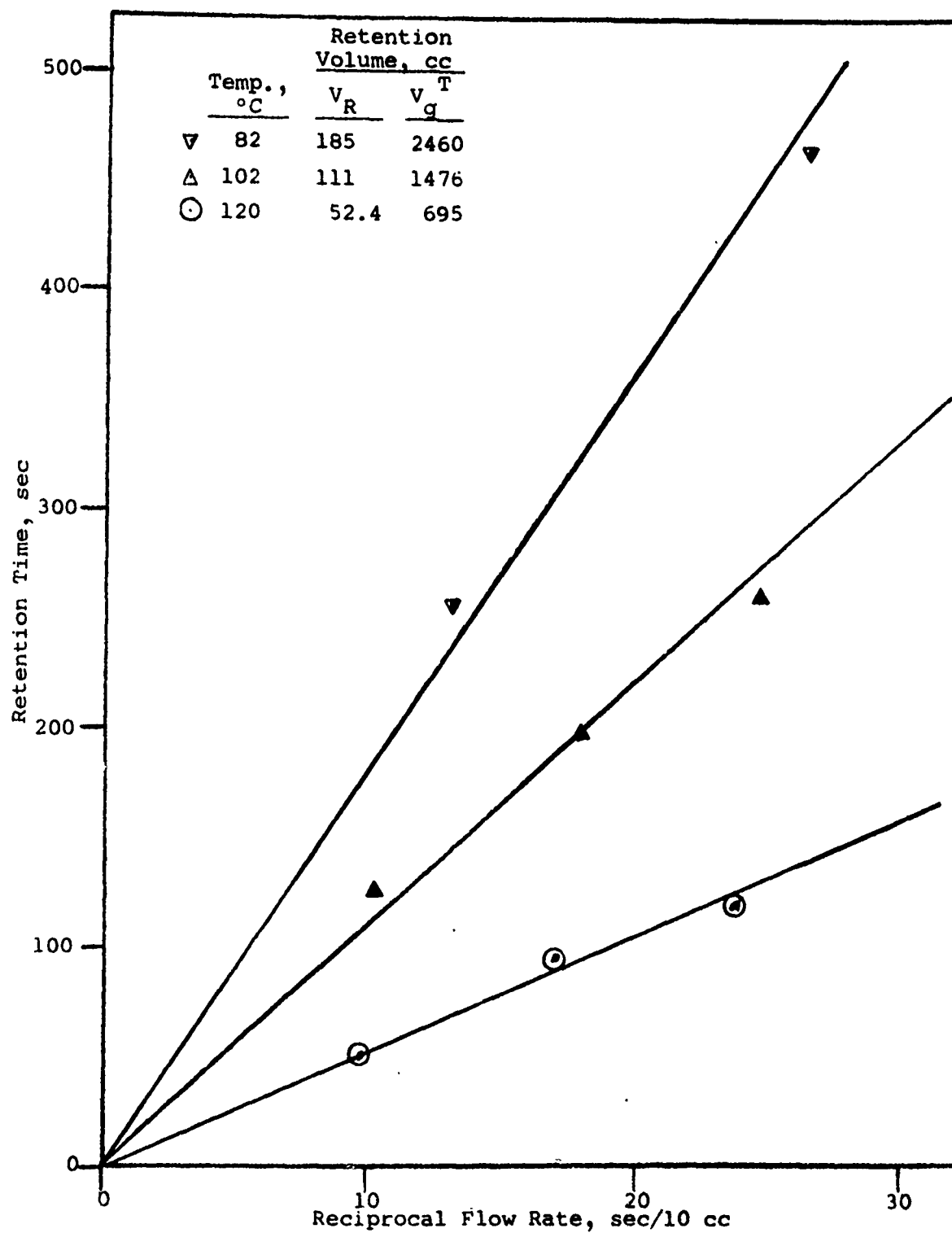


FIGURE 20 - Retention of Nitrobenzene by Carotene-Doped Apiezon-N Grease

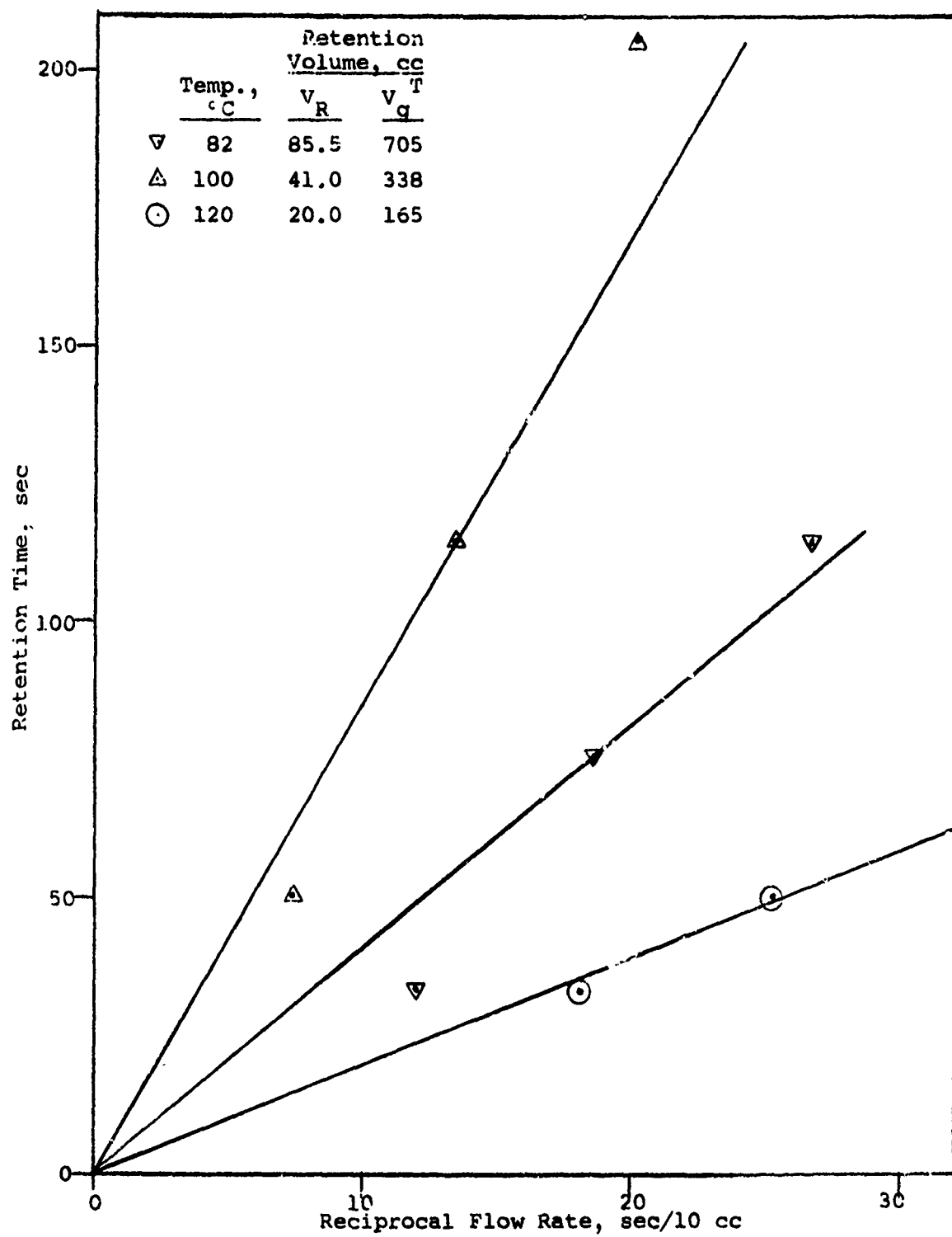


FIGURE 21 - Retention of EGDN by Biliverdin-Doped Apiezon-N Grease

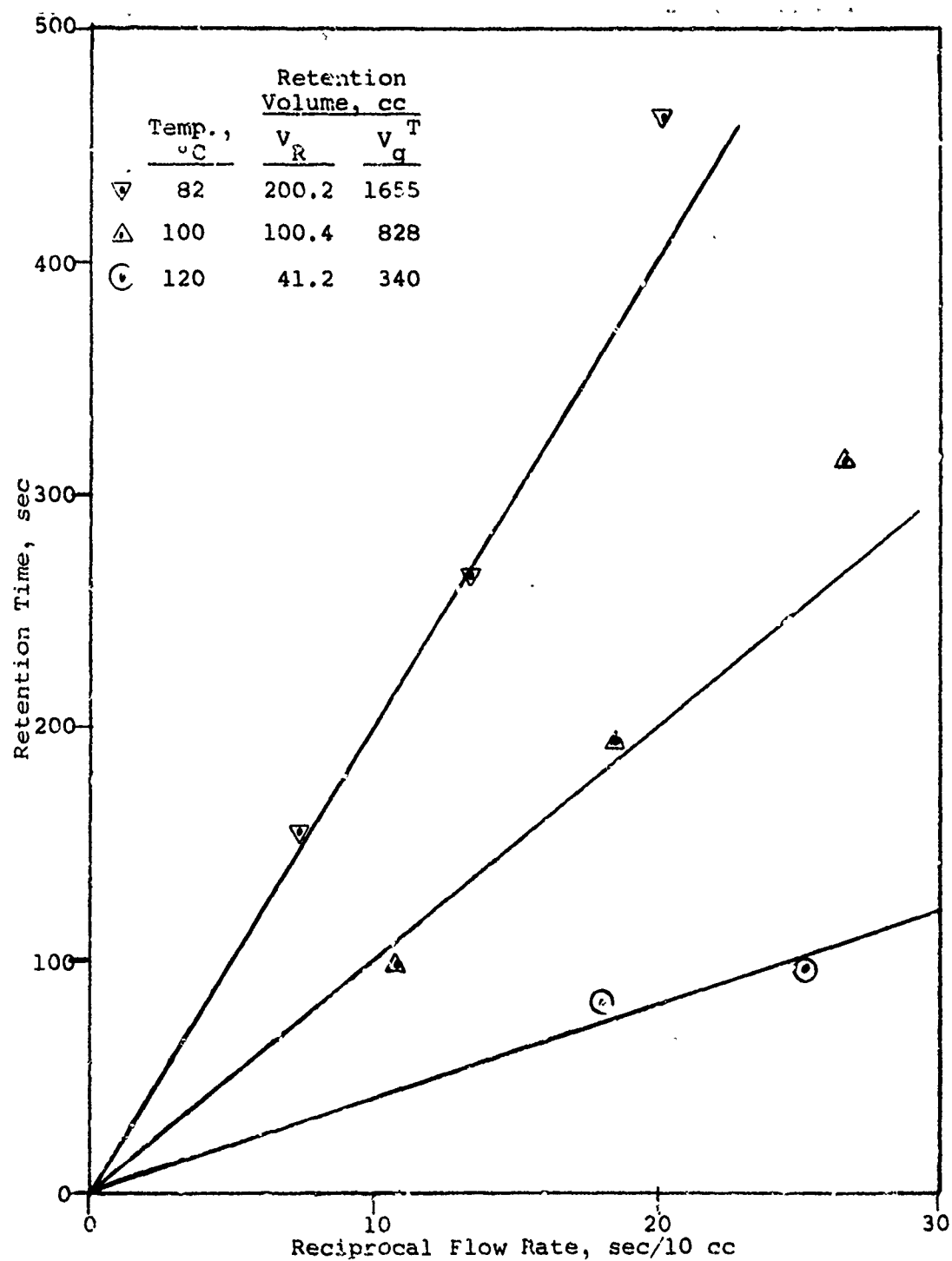


FIGURE 22 - Retention of Nitrobenzene by Biliverdin-Doped Apiezon-N Grease

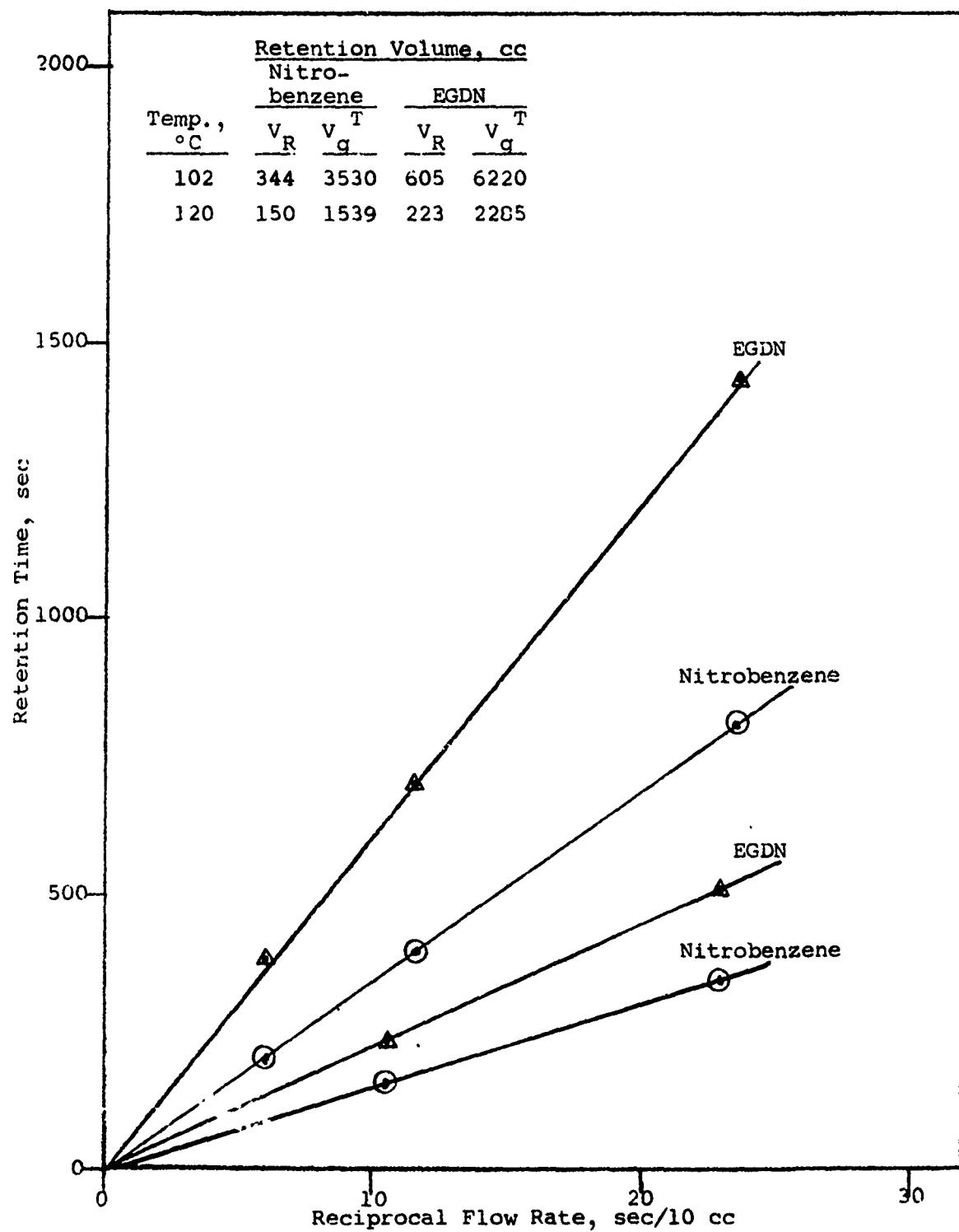


FIGURE 23 - Retention of EGDN and Nitrobenzene by Carbowax 4000

The other coatings studied were: slightly polar squalene, more polar Silicone Ester-52 and dinonyl phthalate, and almost nonpolar Kel-F grease. The data for these materials are presented in Figures 24 through 31.

2.3.7 Effect of High Pressure

In a recent paper, Giddings et al (ref. 4) report rapid (less than 1 min), efficient separations through the use of high pressure. To test this idea, a series of experiments was performed with the column and the detector placed in a 2-in.-OD common water pipe. The pipe was fitted with end caps, and was drilled and tapped for an inlet and an outlet and electrical connections to the detector. After assembly, the pipe was wrapped with asbestos and Nichrome wire to provide heating.

The column was 1/8-in. OD Teflon tubing 14 in. long, packed with 0.115 g of shredded Teflon coated with Apiezon-L to 10% by weight. Apiezon-L is similar to Apiezon-N but is lower in molecular weight. The column was attached to the injection block through a 1/8-in.-OD stainless-steel tube. This was necessary because Teflon bursts under high pressures. The injection block tee, one port of which was covered by a silicone rubber plug through which the injection needle was inserted, had to be slightly modified to withstand the high pressure. This was done by placing a metal washer having a 0.040-in. hole drilled through it between the retaining nut and the rubber septum. The hole was small enough to prevent rubber from rupturing until the pressure was very high. It worked well at 130°C and 300 psig.

EGDN was injected at three different external flow rates at pressures starting at room pressure, about 15 psia. Pressure steps of 15 psi were studied up to 90 psia. The data are shown in Figure 32, in which the delay time of the EGDN peak is plotted versus the reciprocal flow rate corrected for pressure and temperature. As can be seen in the figure, the delay time became longer and longer as the pressure was raised. All the data lie nearly on a straight line through the origin, as required (see Section 2.3.1).

In a later experiment the pressure was raised to 300 psig and several injections were made. The resultant peaks were very broad and flat, because the retention time was several minutes. We concluded that high-pressure operation had no important advantages for our purposes and therefore discontinued further work. However, we will keep in mind the possibility of using pressure as a controllable variable.

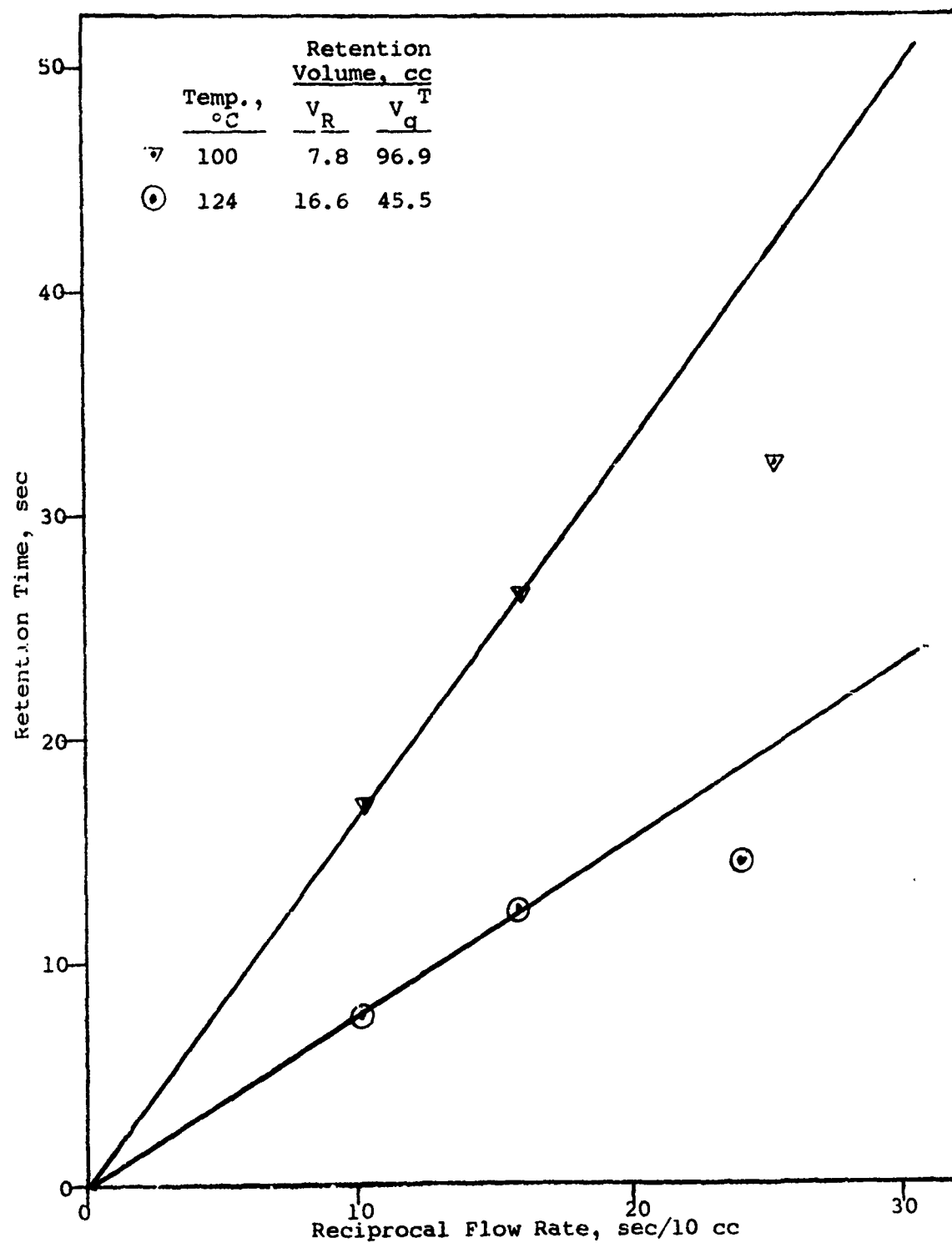


FIGURE 24- Retention of EGDN by Squalene

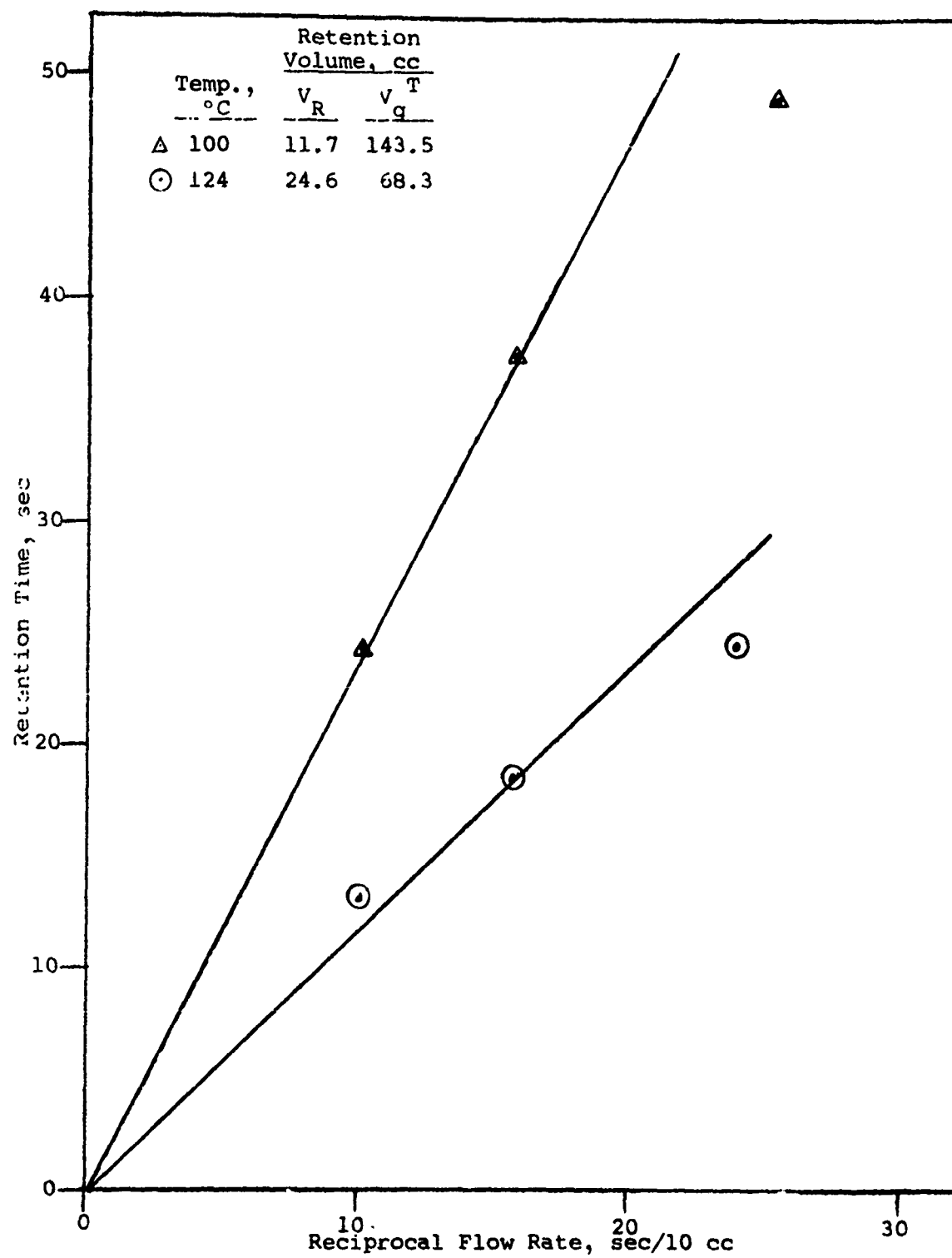


FIGURE 25 - Retention of Nitrobenzene by Squalene

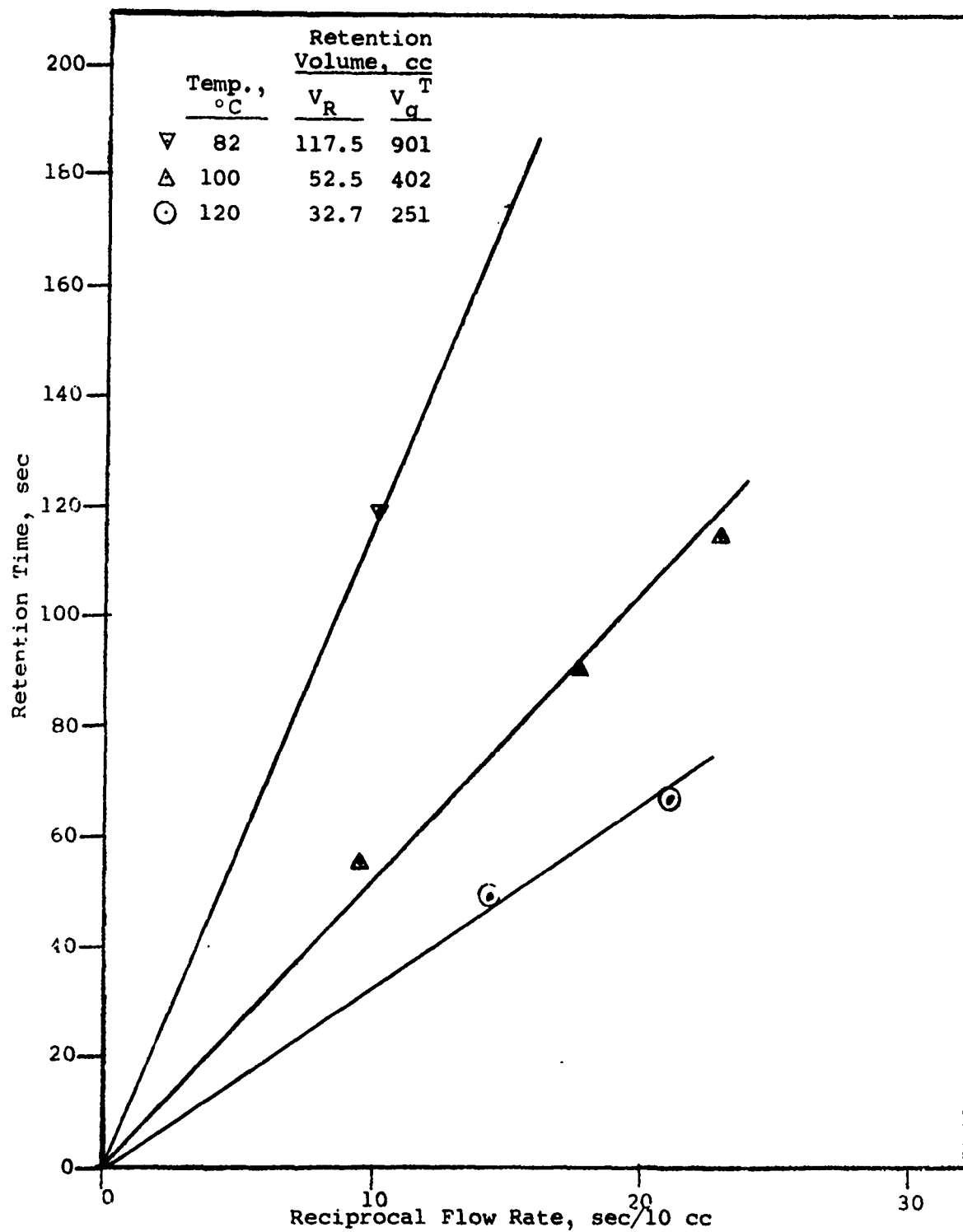


FIGURE 26 - Retention of EGDN by Silicone Ester-52

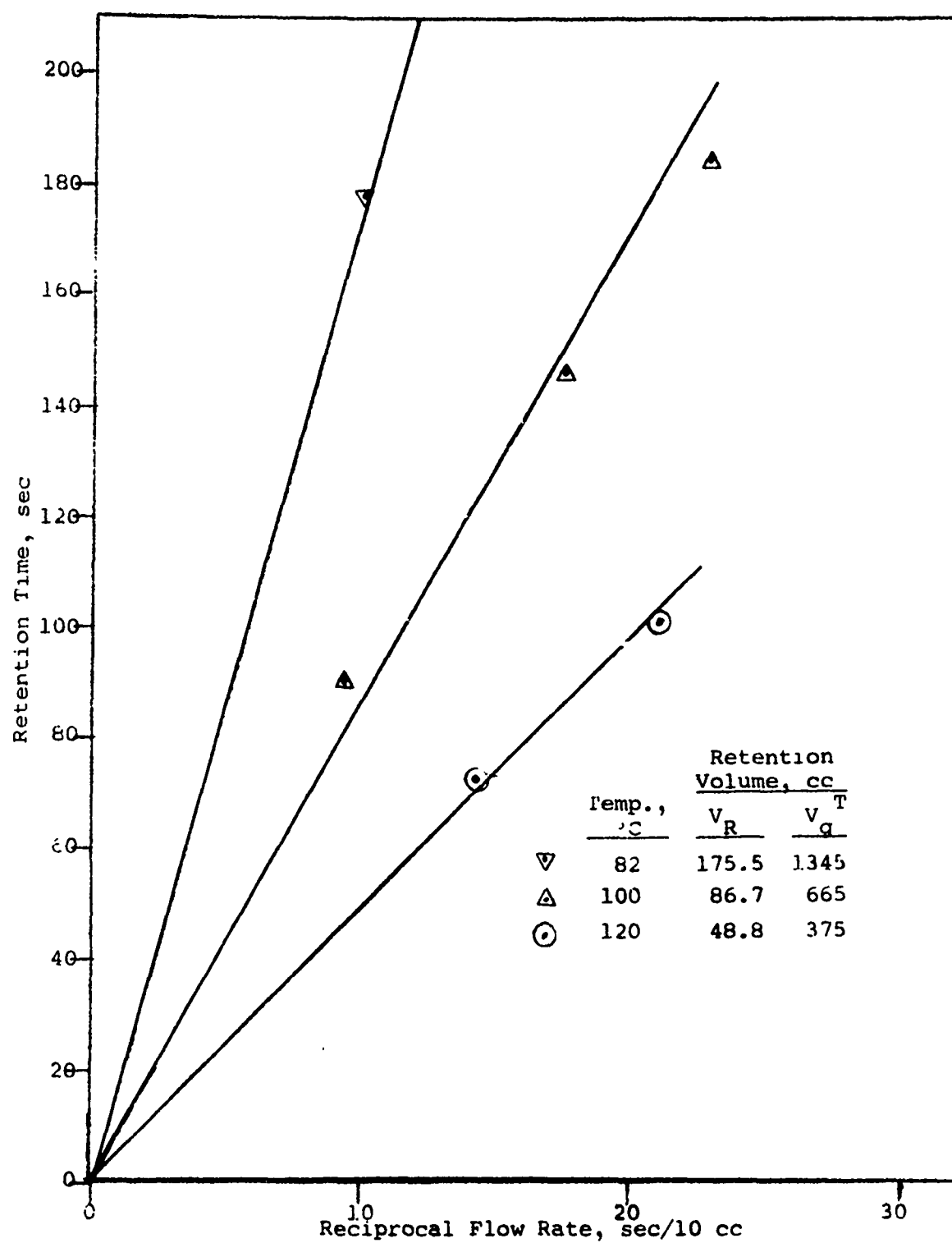


FIGURE 27 - Retention of Nitrobenzene by Silicone Ester-52

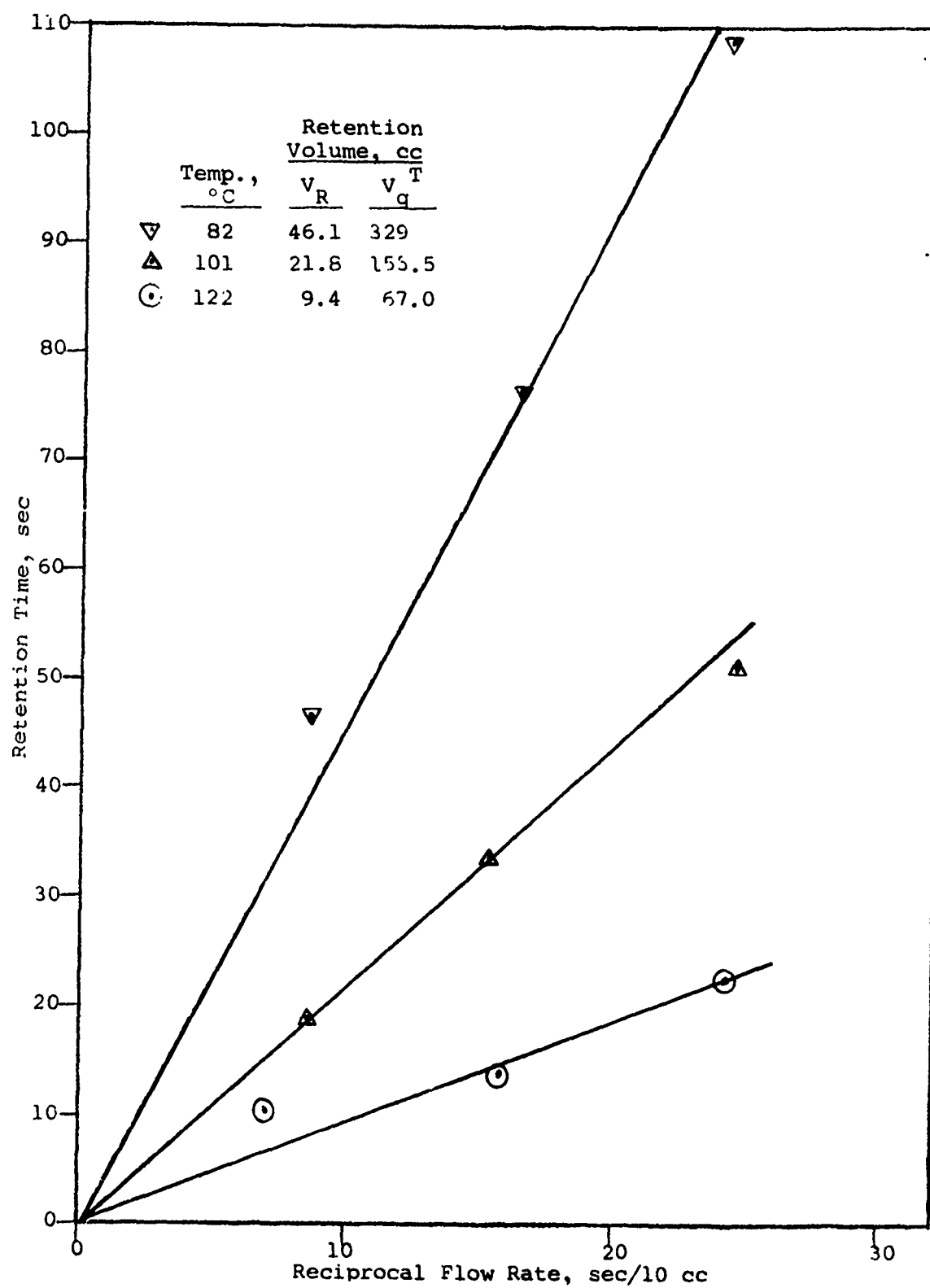


FIGURE 28 - Retention of EGDN by Dinonyl Phthalate

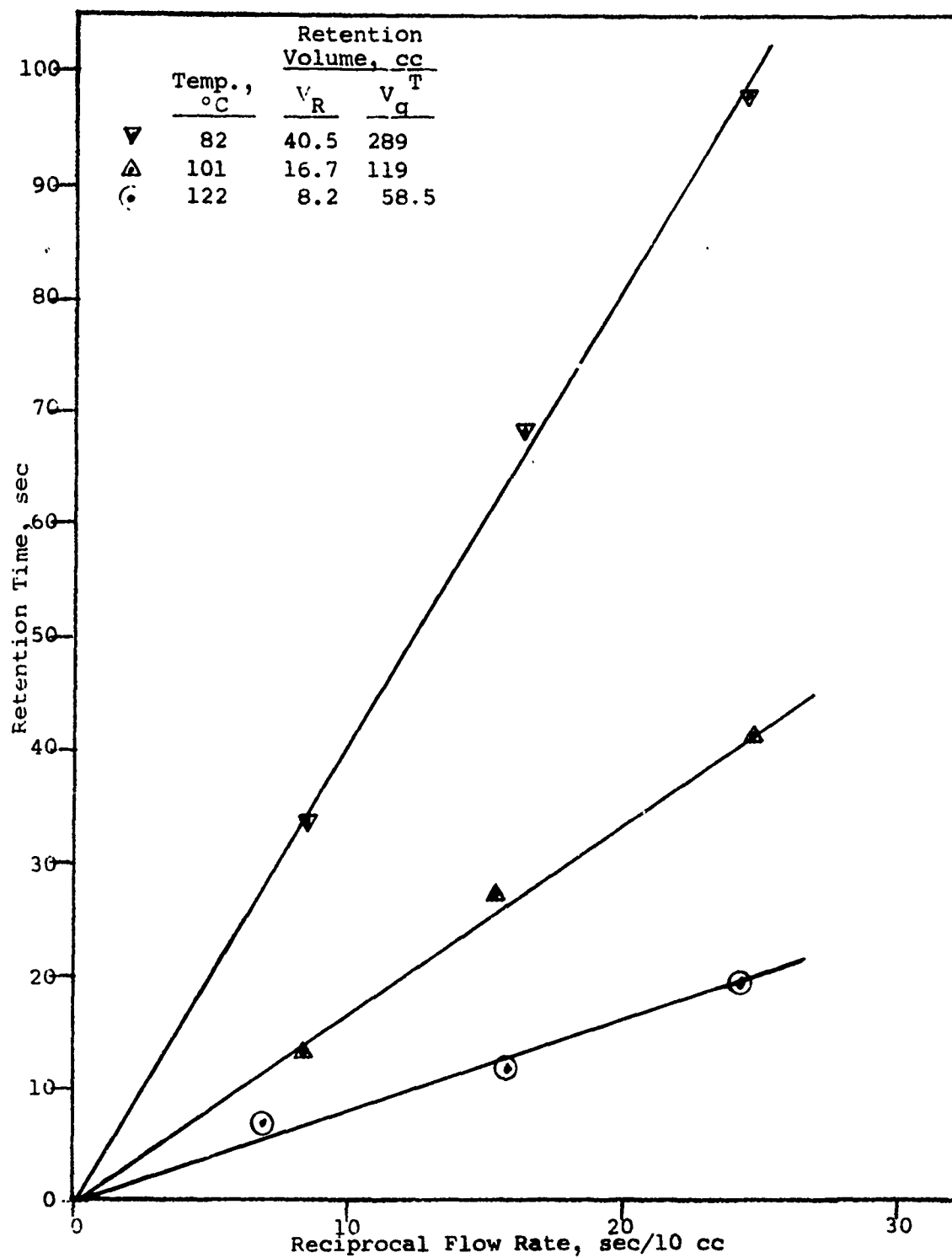


FIGURE 29 - Retention of Nitrobenzene by Dinonyl Phthalate

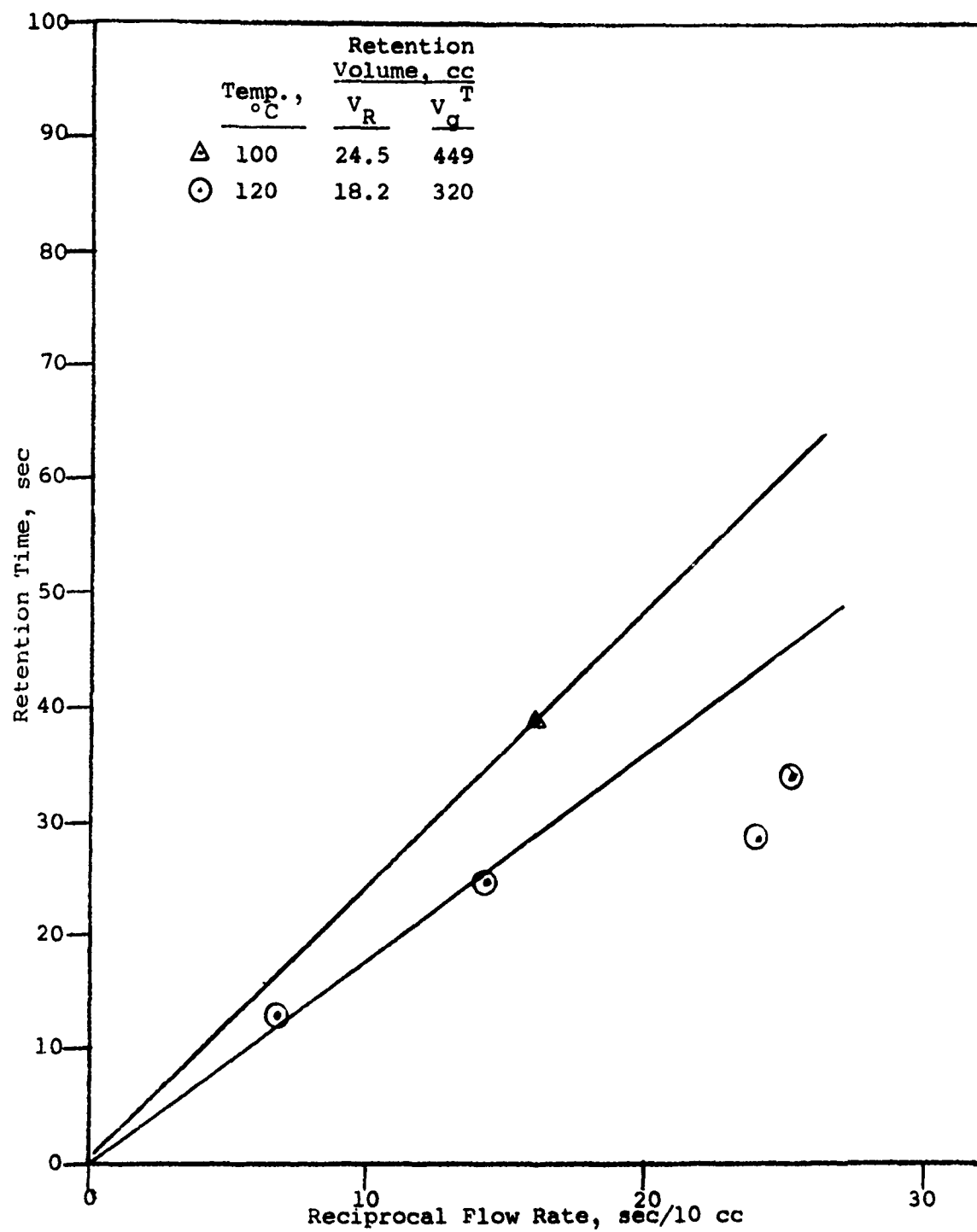


FIGURE 30 - Retention of EGDN by Kel-F Grease

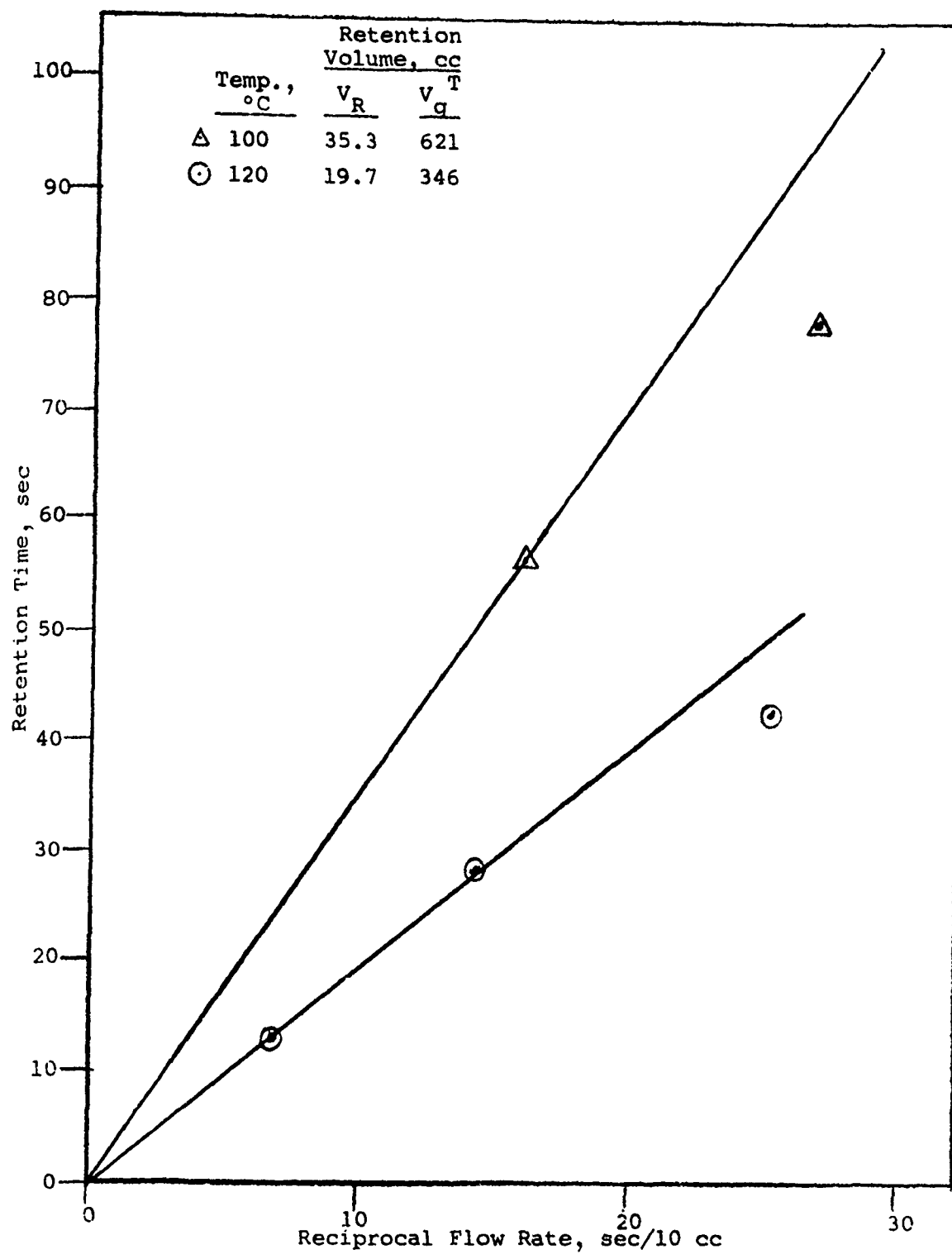


FIGURE 31 - Retention of Nitrobenzene by Kel-F Grease

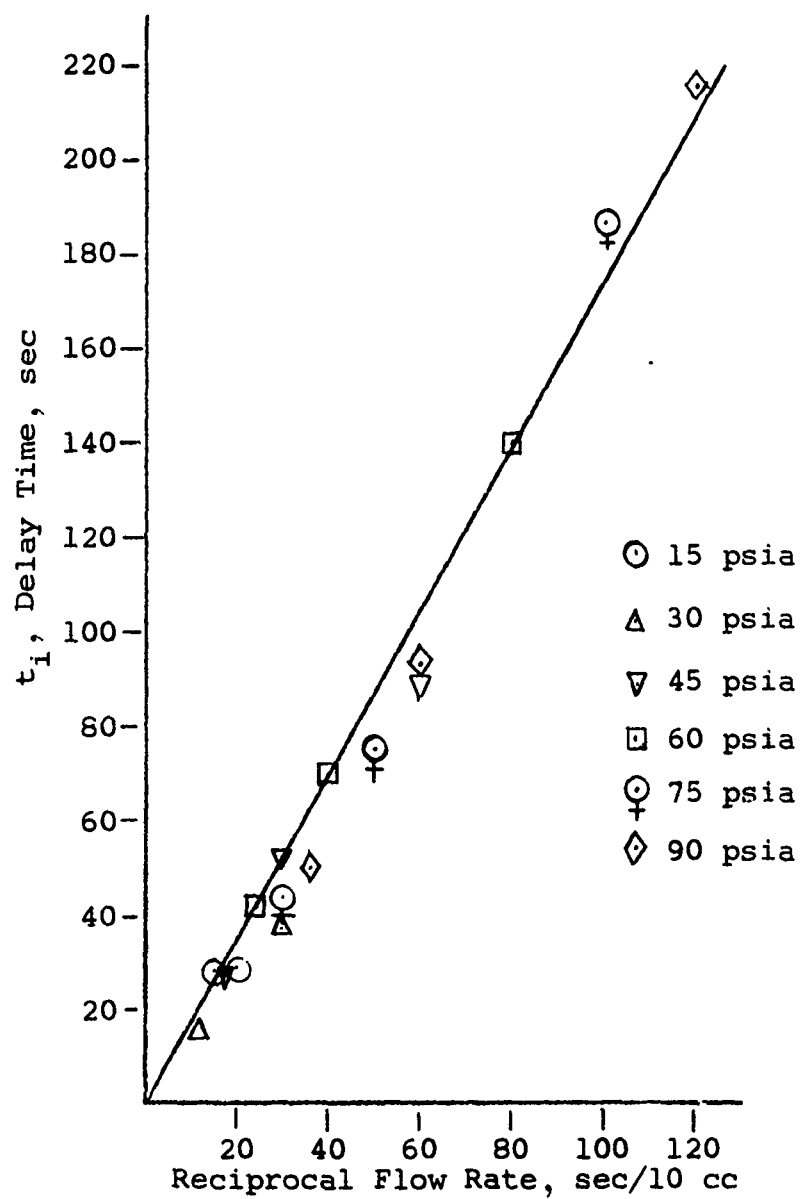


FIGURE 32 - Delay Time for EGDN versus Reciprocal Flow Rate at Various Pressures

2.3.8 Summary

The data relating to flow rate, temperature, coating type, and amount of coating can be conveniently summarized through the use of certain thermodynamic relations as applied to chemical systems.

In a recent paper on the thermodynamics of solutions by gas chromatography, Langer and Purnell (ref. 5) used the following definitions and relations:

V_g^T , retention volume of vapor per gram of stationary phase corrected for gas volume and temperature, cc

M , molecular weight of stationary phase, g/mole

p° , vapor pressure of vapor at temperature of the column, mm Hg

γ^i , activity coefficient of vapor at infinite dilution, unitless

R , gas constant, 62,360 mm_{Hg}·cm³/mole·°K, or 1.987 cal/mole·°K

T , temperature, °K

ΔG_e^i , Gibb's excess free energy function at infinite dilution, cal/mole.

The activity coefficient is calculated from V_g^T , M , p° , R , and T by the relation

$$\gamma^i = \frac{R T}{M p^\circ V_g^T} \quad (6)$$

V_g^T is obtained from the flow rate and the delay time of the peak of the vapor concentration curve divided by the amount of liquid coating present. p° is obtained from a plot of vapor pressure versus reciprocal temperature (Figure 32). M is obtained from the structural formula of the stationary phase. T is the temperature of the column.

The Gibb's excess free energy is calculated from the following relation:

$$\Delta G_e^i = 2.303 R T \log_{10} \gamma^i \quad (7)$$

Generally, the retention times of EGDN and nitrobenzene were measured at three different temperatures, approximately 82, 101, and 120°C. Hence, ΔG_e^i calculated from Equations 6 and 7 can be plotted versus temperature and a smooth curved drawn through the points. These curves can then be used to calculate retention volumes for EGDN at any intermediate or slightly higher or lower temperatures. Actual retention times can be determined from these data by dividing the resulting retention volume by the flow rate. In this way, full use of the data for future development of columns is possible.

As an illustrative calculation, Table V was constructed for an Apiezon-N column containing a total mass of 0.02 g of grease and assuming a flow rate of argon carrier gas 30 cc/min.

TABLE V - Use of Gibbs Free Energy for Tailormaking an Apiezon-N-Coated Column

Temp., °K	ΔG_e^i , cal/mole	γ^i	p° , mm Hg	V_g^T , cc	R_T , sec
350	820	3.25	4.5	1165	46.6
360	648	2.47	9.0	787	31.4
380	300	1.49	27.0	460	18.4

R_T for a corrected flow rate of 30 cc/min and 0.02 g total weight of Apiezon-N on Teflon shreds.

Similar calculations can be made for the other coatings if it is necessary to design a new column to separate EGDN from some interfering substance.

The variations of ΔG_e^i with temperature for EGDN and nitrobenzene for the various coatings are shown in Figures 33 through 40.

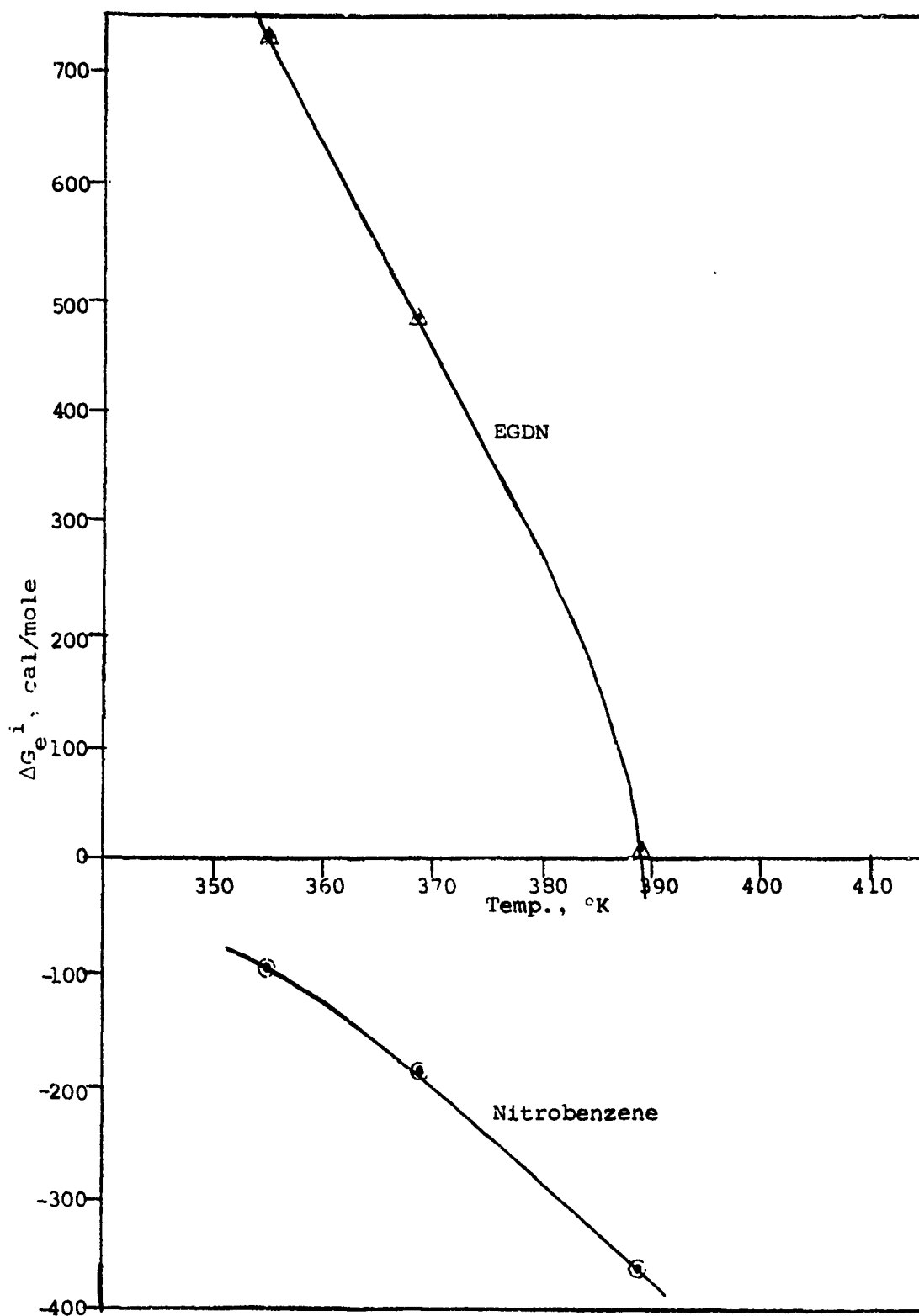


FIGURE 33 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Apiezon-N

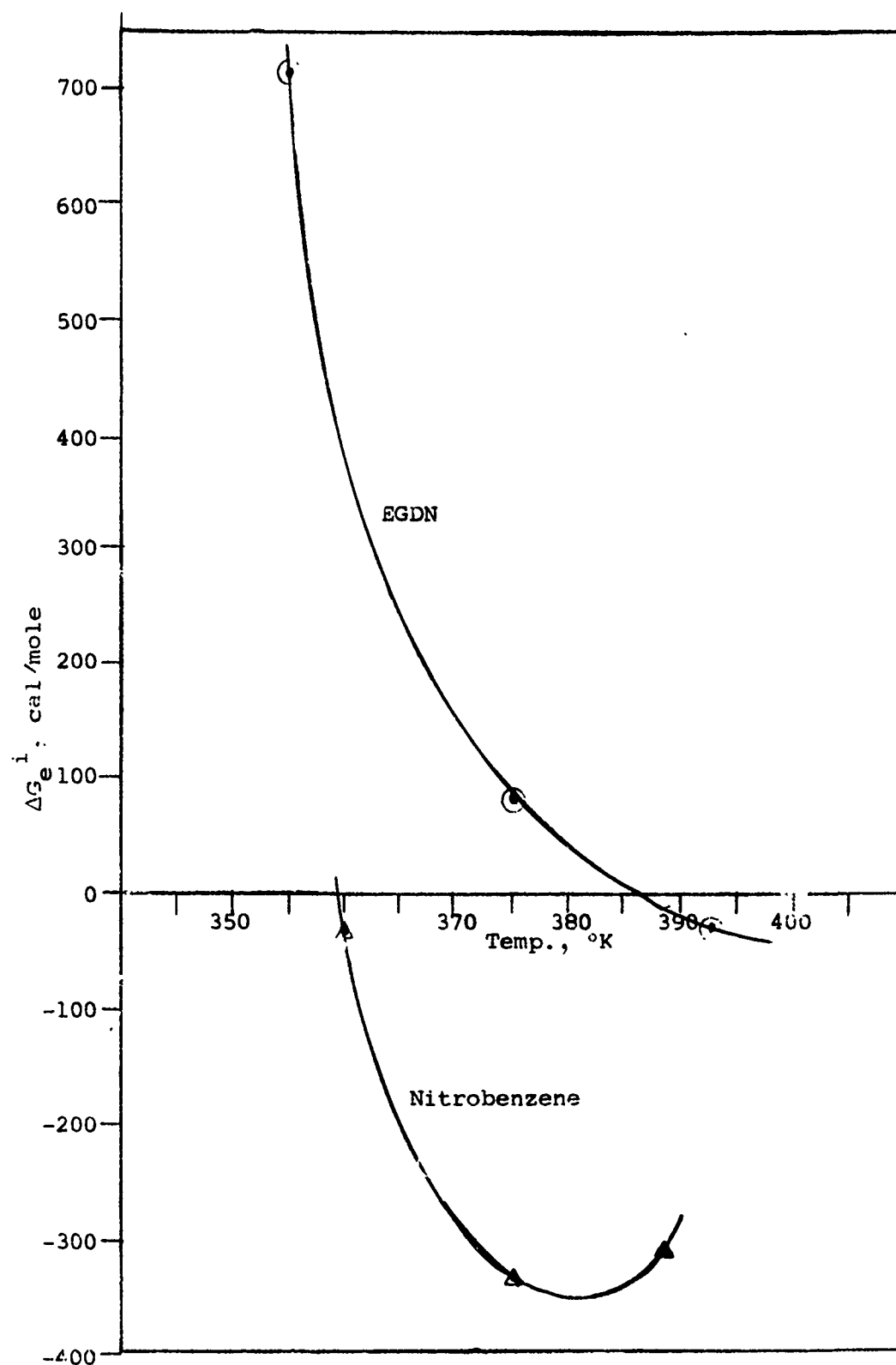


FIGURE 34 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Carotene-Doped Apiezon-N

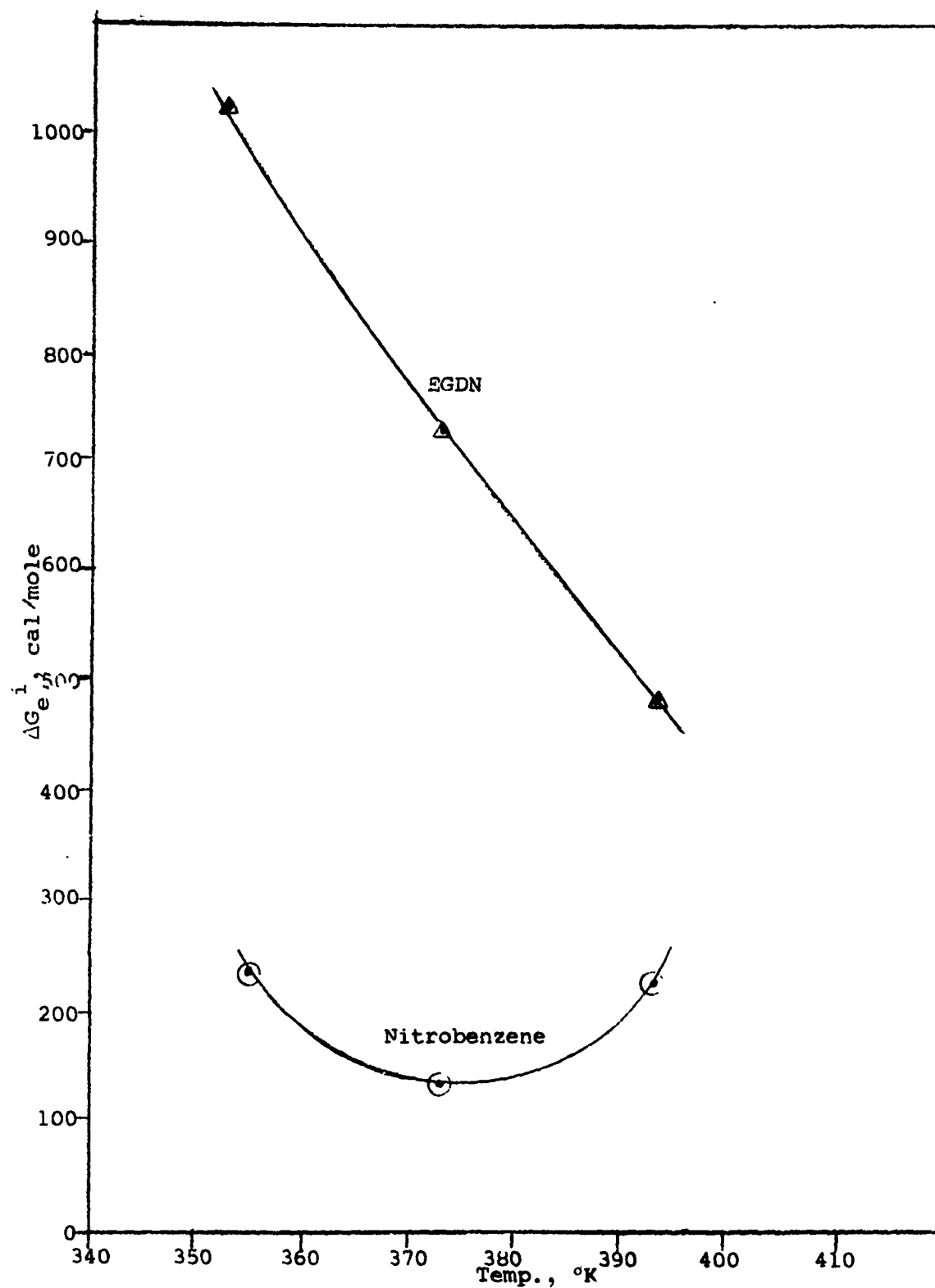


FIGURE 35 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Biliverdin-Doped Apiezon-N

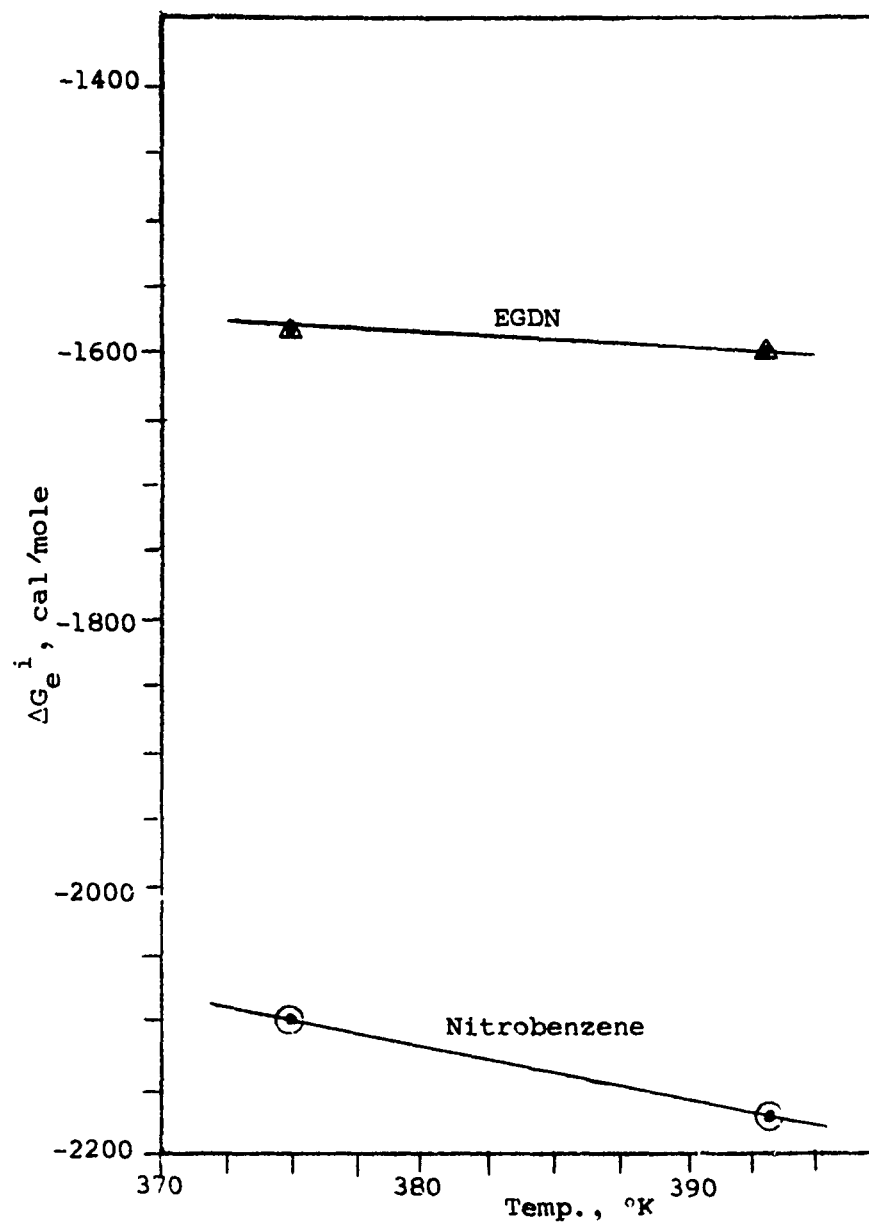


FIGURE 36 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Carbowax 4000

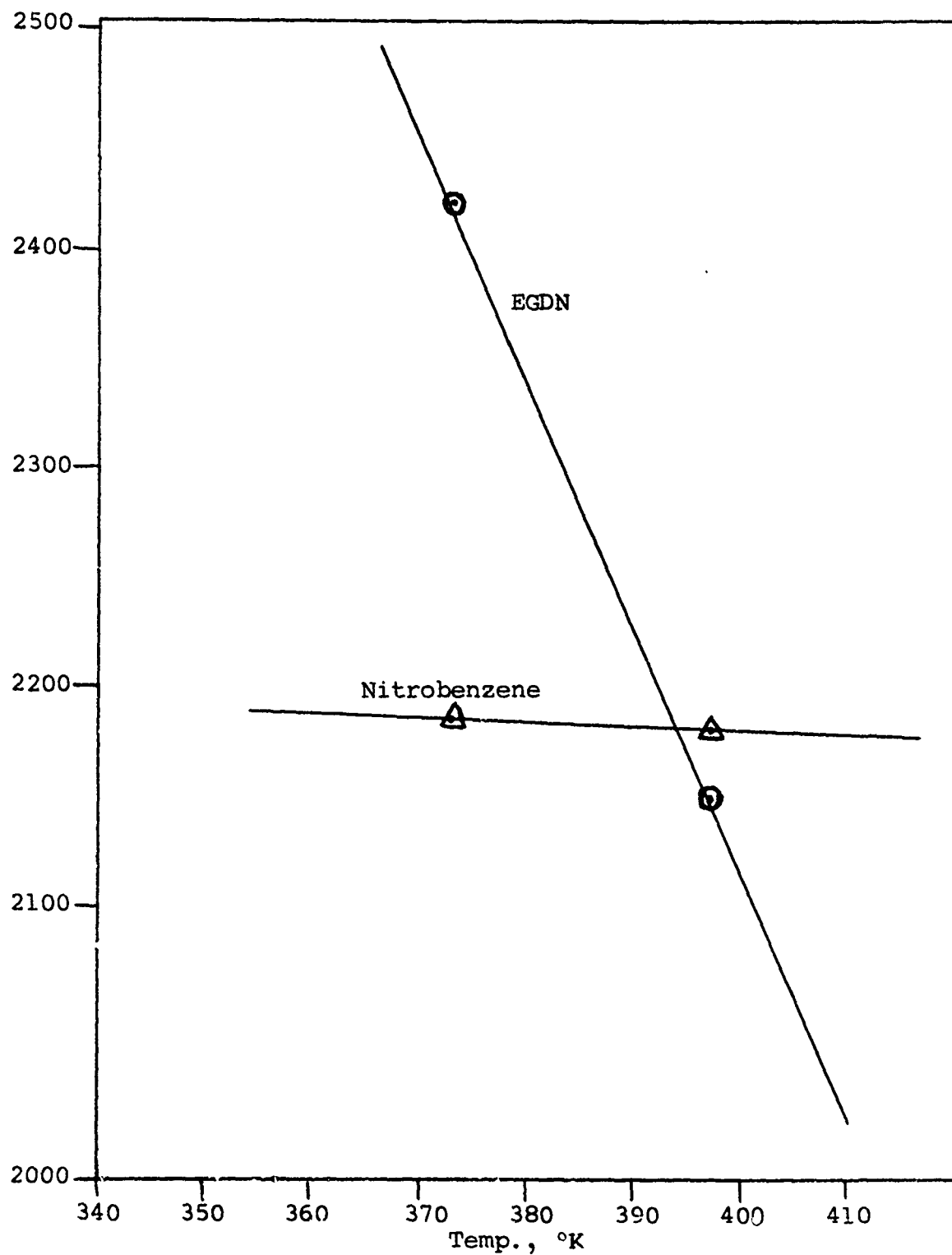


FIGURE 37 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Squalene

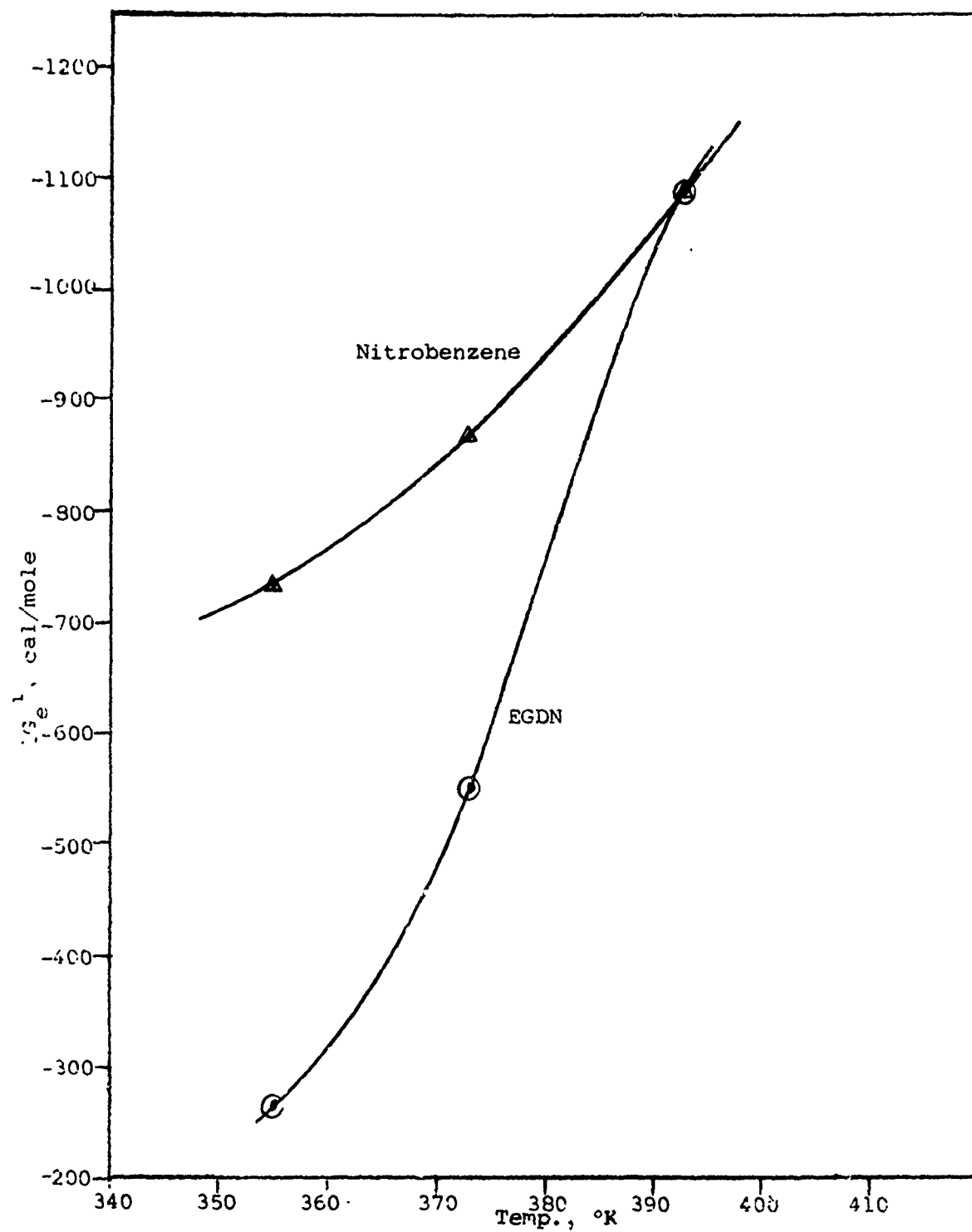


FIGURE 38 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Silicone Ester-52

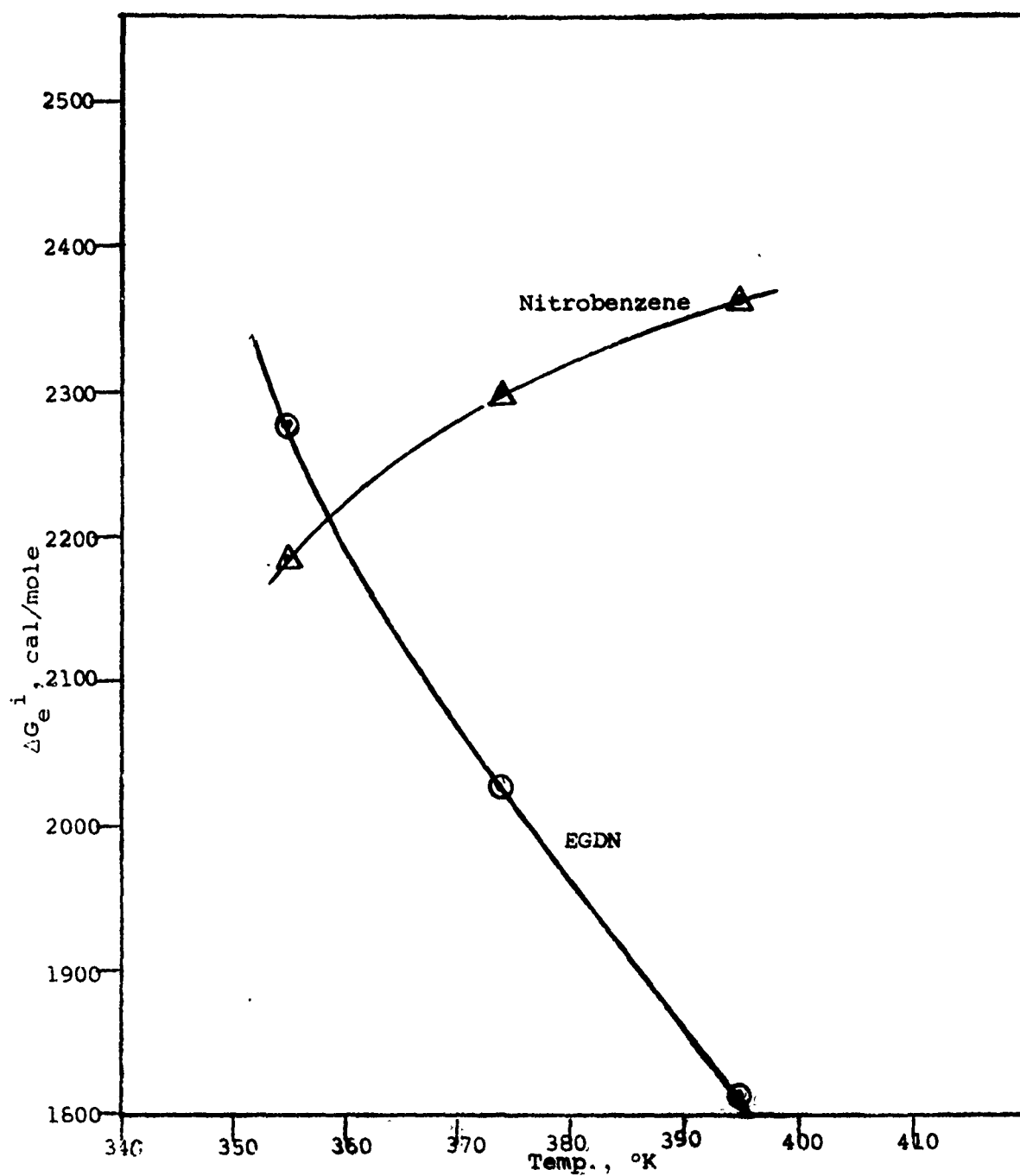


FIGURE 39 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Dinonyl Phthalate

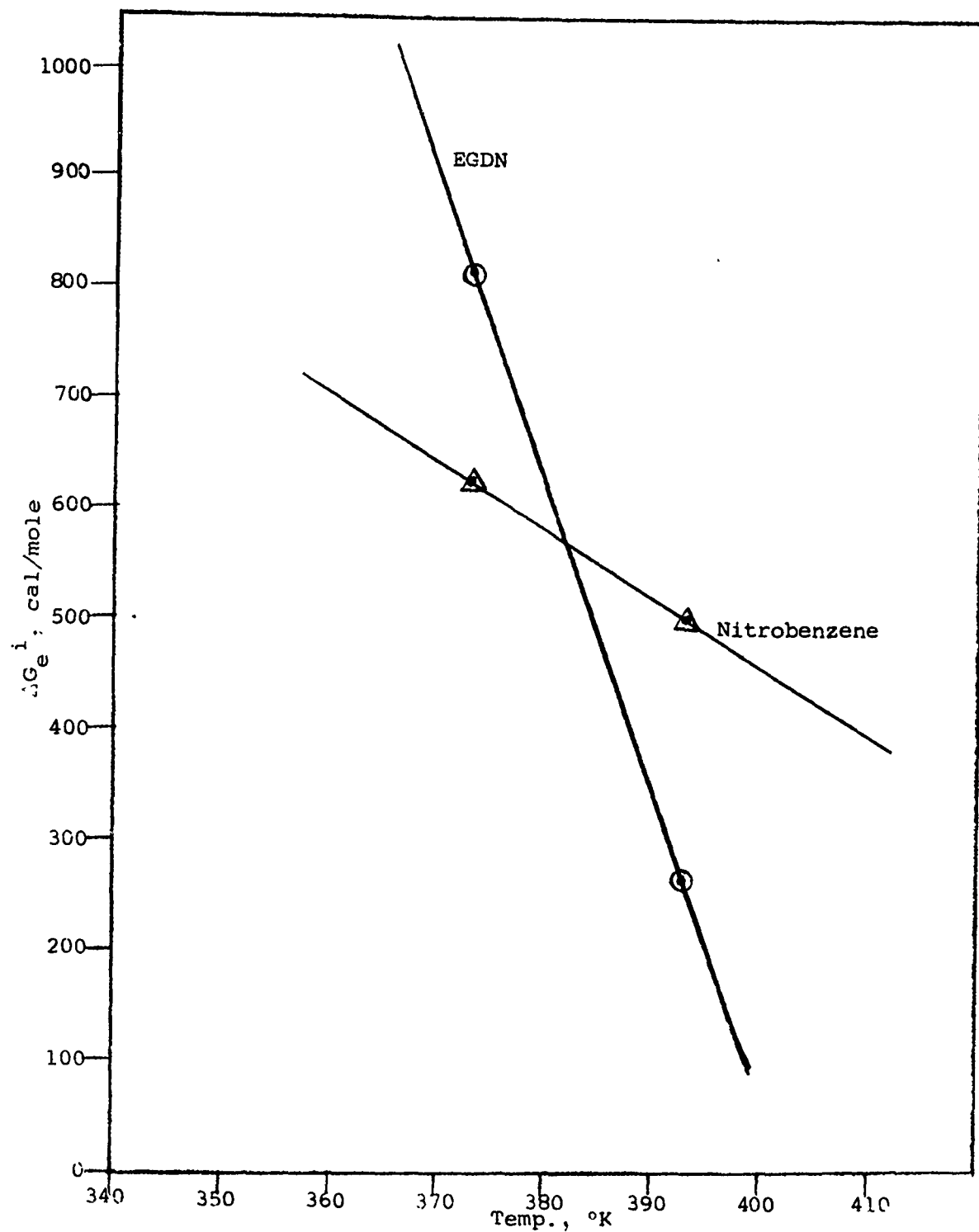


FIGURE 40 - Gibbs Excess Free Energy versus Column Temperature for Separation of EGDN and Nitrobenzene on Kel-F Grease

2.4 Collection of Explosive Vapors

There are numerous techniques for collection of air samples. The most obvious method is to pass air through a cold tube and thereby completely condense most of the vapors. The disadvantage of this and similar methods is that unwanted vapors (mainly water vapor) are removed, dilute the pertinent vapors, and thus little gain results.

Early in our study of EGDN vapors we noted that the metal needles of our sampling syringes seemed to retain vapors on their surfaces. This process, called "adsorption" to distinguish it from "absorption," is a surface phenomenon in which molecules in the vapor phase are retained on a surface.

The surfaces of liquids are in a state of imbalance (or unsaturation), as evidenced by the phenomenon of surface tension. The same is also true of solid surfaces, on which the molecules or atoms do not have all their forces satisfied by union with other particles. Consequently, solid surfaces tend to satisfy their residual forces by attracting onto and retaining on their surfaces gases or dissolved substances with which they come into contact. The gas (or vapor) adsorbed is called the "adsorbed phase," and the solid is called the "adsorbent."

Generally, the amount of vapor that can be adsorbed on a surface depends on the natures of the solid and the vapor, on the surface area of the adsorbent, on the temperature of the system, and on the pressure of the adsorbate.

Figure 41 is a typical adsorption isotherm for a material, that upon forming an adsorbed layer, releases energy of 5 to 10 kcal/mole greater than its heat of vaporization. The isotherm is a plot of surface concentration or other equivalent unit proportional to surface concentration versus relative pressure of the adsorbate. It is called an "isotherm" because the data are for a particular temperature.

Extrapolation of the straight portion of the curve in the range of 0.1 to 0.4 relative pressure to the ordinate gives the point M at zero relative pressure. This point represents the approximate amount of material needed to form a single layer of adsorbate (monomolecular layer). Generally, a monolayer forms when the relative pressure is about 0.1, i.e., the pressure of the vapor is about 10% of the saturation vapor pressure.

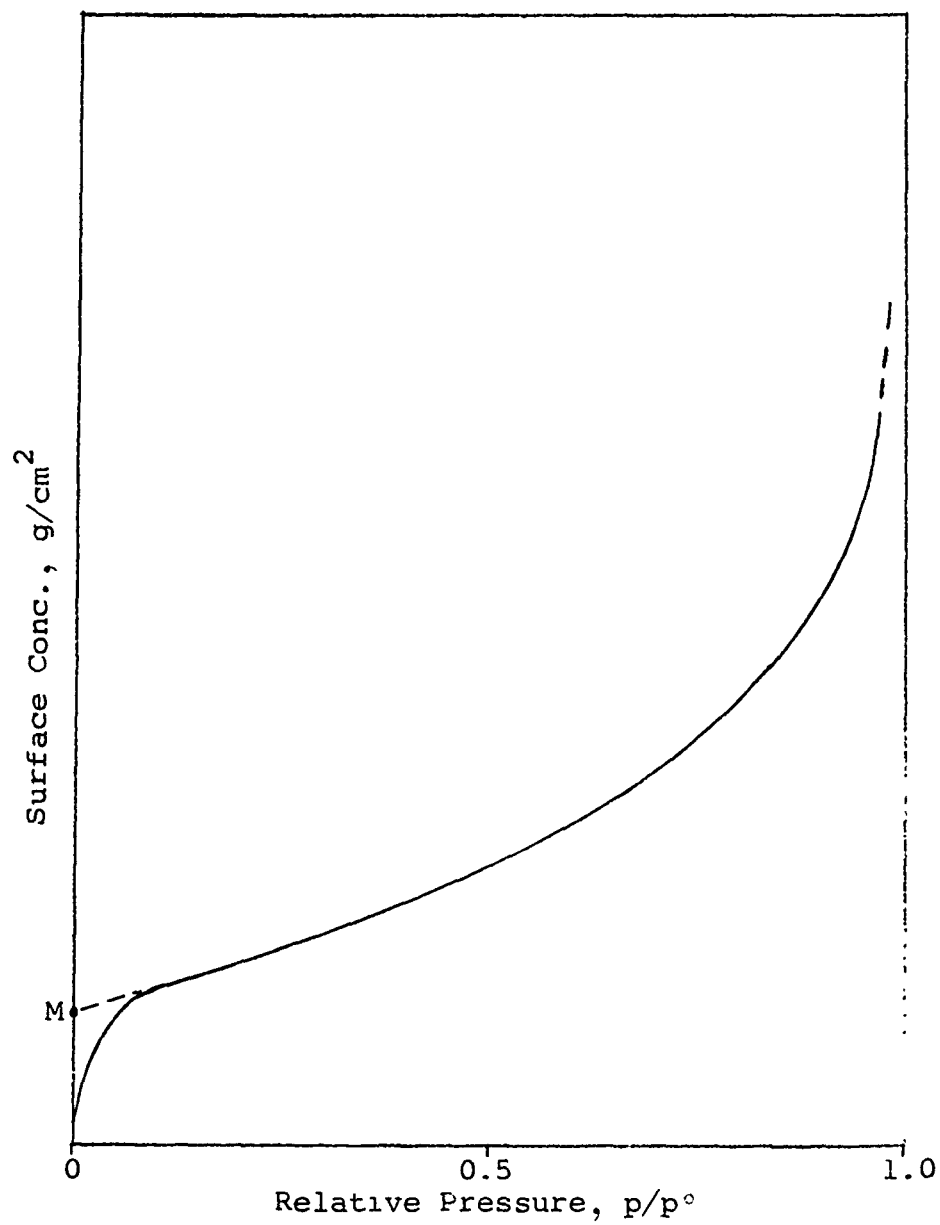


FIGURE 41 - Type II Adsorption Isotherm

Qualitative observation of Figure 41 indicates that vapors showing a definite interaction with a surface tend to form a monolayer at low relative pressures, remain fairly uniform at intermediate relative pressures, and form thick layers only at very high relative pressures, near 1.0.

This behavior can be understood on the basis of the molecular structure of materials. As soon as a monolayer is formed, most of the unsaturated forces at the solid surface are satisfied. Thus, little further surface energy is available to form the second and subsequent layers. Only when the relative pressure is fairly high and the vaporous material is on the verge of condensing to a liquid are thick layers formed.

The next most important parameter is temperature. Generally as the temperature is raised, the interactions of the vapor and the solid surface grow weaker. At the same time, the vapor pressure, p^0 , increases exponentially; this is the more important of the two effects. A constant pressure, p , of a vapor means that as the temperature increases, the relative pressure, p/p^0 , becomes smaller and smaller. From Figure 41 it is evident, then, that the amount of vapor that can be adsorbed, i.e., the surface concentration, must decrease drastically as the temperature is increased.

To use these effects as a sample collection and separation system, an adsorbent must be found that strongly retains the explosive vapors (EGDN) in the presence of normal atmospheric components (oxygen, water vapor, and carbon dioxide) as well as other contaminants. Further, the adsorbent should release the vapors upon moderate heating without causing excessive decomposition or other changes in molecular structure.

Since the stainless-steel surface of our sampling needles was known to adsorb EGDN and nitrobenzene vapors with some effectiveness, we decided to study it and several other metal surfaces on a directly comparative basis. The results are reported in the following sections.

2.4.1 Adsorption on Metal and Other Tubes

At the time these experiments were devised, we were contemplating a final adsorption sample collection system consisting of a large bundle of parallel tubes perhaps 12 in. long. As it turned out, a quite different geometrical arrangement, based primarily on the secondary heating requirements, was finally devised.

To compare different adsorptive surfaces, then, various tubes approximately 12 in. long, 1/8 in. OD, and of varied ID, as listed in Table VI, were prepared or obtained from the listed sources. These were placed in a 15-in.-long by 2-in.-OD heated thick-walled copper cylinder in front of the column injection block, as shown in Figure 42. With this system, the retention of like amounts of EGDN vapors could be studied as they moved through either the column alone (by injection through the column injection block) or through both the column and the collection tube (by injection upstream of the collection tube).

TABLE VI - Dimensions and Sources of Adsorption Tubes

Metal	Length, in.	OD, in.	ID, in.	Source
303 Stainless steel	13.5	0.125	0.0512	Superior Tube Co. Norristown, Pa.
Copper (dehydrated)	13.5	0.125	0.0650	Harry Alter Co. Chicago, Ill.
Teflon	15	0.125	0.0670	Cadillac Plastics Co. Chicago, Ill.
Pyrex	12	0.125	0.0710	Stock
Platinum	12	0.125	0.0625	Engelhardt Ind., Inc. Newark, N.J.
Gold	12	0.125	0.0625	Engelhardt Ind., Inc. Newark, N.J.

As in previous work, EGDN samples were obtained by adsorption of dynamite vapors on the needle of a 10- μ l syringe. About 5 μ l of air was also introduced, in order to have a reference peak (oxygen) prior to the EGDN peak. This allowed direct comparison of the effect of the collection tube, since the delay time of the combined tubes could be measured by the distance between the air peak and the EGDN peak. This automatically accounts for the small extra delay due to the added volume of the collection tube over that of the separation column itself.

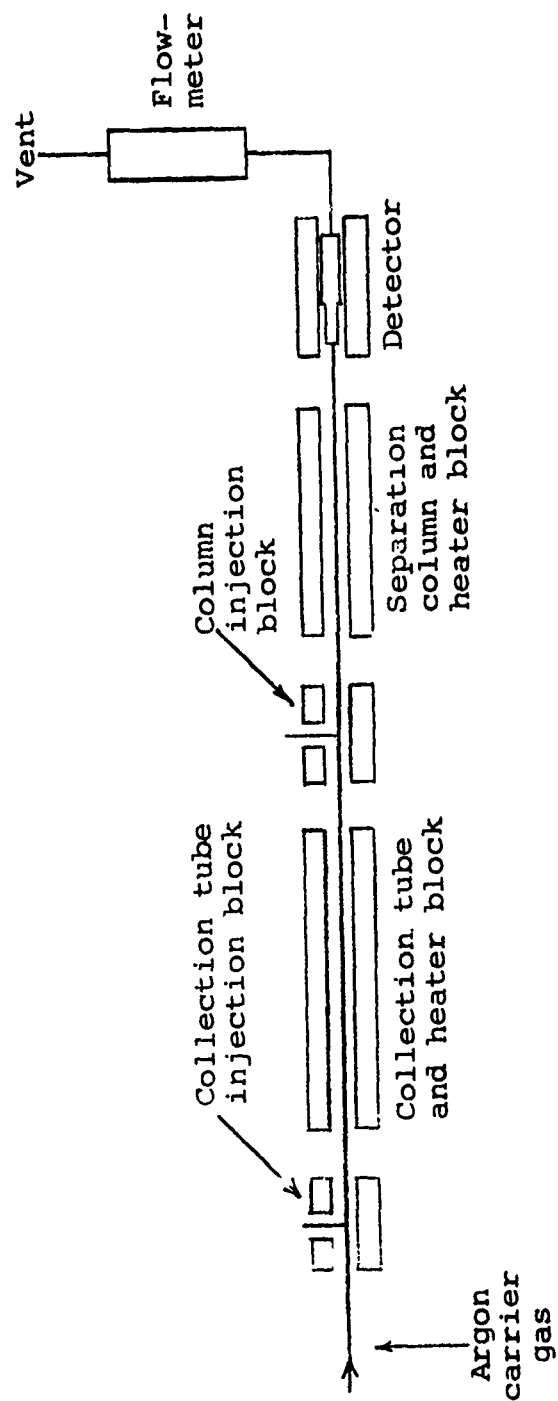


FIGURE 42 - Apparatus for Studying Adsorption on Various Surfaces

Measurement of the areas of the EGDN peaks allows a rough estimate of the amount of decomposition caused by the combined effect of the tube surface and its temperature. Because of its explosive nature, EGDN is naturally sensitive to high temperature. As is illustrated by the following data, serious decomposition of the EGDN resulted above about 150°C in all cases.

The results of these experiments and measurements are outlined in Tables VII and VIII. The collection tube injection block, the column injection block, and the detector were held at 140°C. The column was at 80°C, and the flow generally about 30 cc/min. The carrier gas was nitrogen.

Examination of Table VII shows that at 0°C complete adsorption occurred on metal tubes and some delay was introduced even on the very inert Teflon surface. As the temperature was raised, the delay introduced by the tube became less and less, approaching zero at high temperatures. The relative delay approached unity at high temperatures. Notice the very large relative delay on gold tubes at room temperature. This is more than 3-1/2 times larger than any other material tested.

TABLE VII - Relative Delay Times of EGDN
for Various Adsorptive Tubes

Tube Material	0°C	25°C	50°C	100°C	150°C	200°C
Stainless steel	C.A.	1.88	1.00	1.00	1.00	n.a.
Copper	C.A.	1.36	1.17	1.00	1.0	1.0
Teflon	1.83	n.a.	1.07	1.07	1.09	1.0
Platinum	C.A.	1.37	1.05	1.00	1.15	1.06
Gold	C.A.	7.1	2.5	1.75	Decomp.	Decomp.

C.A., complete adsorption.

n.a., not available.

Decomp., decomposed.

In Table VII the ratios of the area of an EGDN peak that passed through the collection tube and the column to the area of a peak through the column only are presented at six temperatures. If there is any decomposition in the metal tube, this ratio should be less than unity. Ratio greater than unity are due to experimental errors. Below room temperature the EGDN was held so tightly in most cases that the peak due to EGDN could not be measured. At temperatures up to 100°C the ratio of peak areas was essentially unity except in the case of gold. Thus little or no decomposition occurred, except in the gold tubes. At temperatures above 150°C definite decomposition of the EGDN occurred, even in the very inert Teflon tubes. In the case of gold, the decomposition was complete at 150°C.

TABLE VIII - Relative Areas of EGDN Peaks

Tube Material	0°C	25°C	50°C	100°C	150°C	200°C
Stainless steel	V.S.	0.96	1.08	1.18	0.54	V.S.
Copper	V.S.	1.1	1.33	0.86	0.95	0.69
Teflon	V.S	n.a.	1.2	1.08	1.11	0.79
Platinum	V.S	1.09	1.00	1.01	0.80	0.55
Gold	V.S	0.30	0.84	0.89	0.0	0.0

V.S., very small.
n.a., not available.

In conclusion, gold surfaces are by far the most adsorptive and therefore the best for collecting and retaining EGDN vapors. However, the temperature at which these vapors can be desorbed is limited to about 100 to 125°C, since gold is so active catalytically that the vapors are decomposed at higher temperatures. Gold is noted for its inertness to water, oxygen, and carbon dioxide and thus presents perhaps a more metal-like surface than other metals. Metals are sometimes treated as rigid lattices of positive charges with a sea of electrons moving about freely in the lattice. Since EGDN is an electron-accepting molecule, it may well be held on gold surfaces by partial transfer of electrons to adsorbed molecules. This process would be partly inhibited in metals

having the usual oxide layer from reaction with air and adsorbed moisture films. Hence the relatively great activity for adsorption and catalytic decomposition of EGDN by gold is qualitatively explained.

2.4.2 Influence of Human-Related Vapors

Since air sampling and analysis for the EGDN vapors must always be conducted where people are present, it was pertinent to explore whether humans evolve vapors that are trapped by gold surfaces, have retention times (in the particular gas chromatographic coating used) similar to those of EGDN, and produce a response in the electron-capture detector. If such vapors occur, the process would have to be modified to resolve the interference.

IIT Research Institute, under Contract No. DA-11-022-MAC-1775(X), with U.S. Army Ballistics Research Laboratory, designed and constructed a glass-Teflon cell in which humans can be temporarily isolated from room air and kept in high-purity air, and the vapors from the humans can be collected and analyzed. A photograph of the equipment is shown in Figure 43. The cell is open, and a human subject is on a Teflon strap platform that can be moved into the glass cell such that the round plate in the middle of the photograph closes the end of the cell with the subject inside.

A white male was placed into the cell, and vapors were passed through a gold tube, 1/8 in. OD by 12 in. long, for 1 hr. The tube was then placed into the gas chromatographic apparatus used for detection of EGDN and flash-heated to 80°C as usual. The gas chromatogram obtained is shown in Figure 44. Although some material was collected, as indicated by an ill-defined hump, no peak that would directly interfere with EGDN was observed.

The test applies to one human subject and indicates only that humans do not necessarily emanate vapors that interfere with the proposed detection process. Vapors from humans differ and depend on diet, state of health, and other factors. Hence, the test does not exclude the possibility of interference in some yet unencountered human vapors. However, it gives a first favorable indication that no interference will occur.

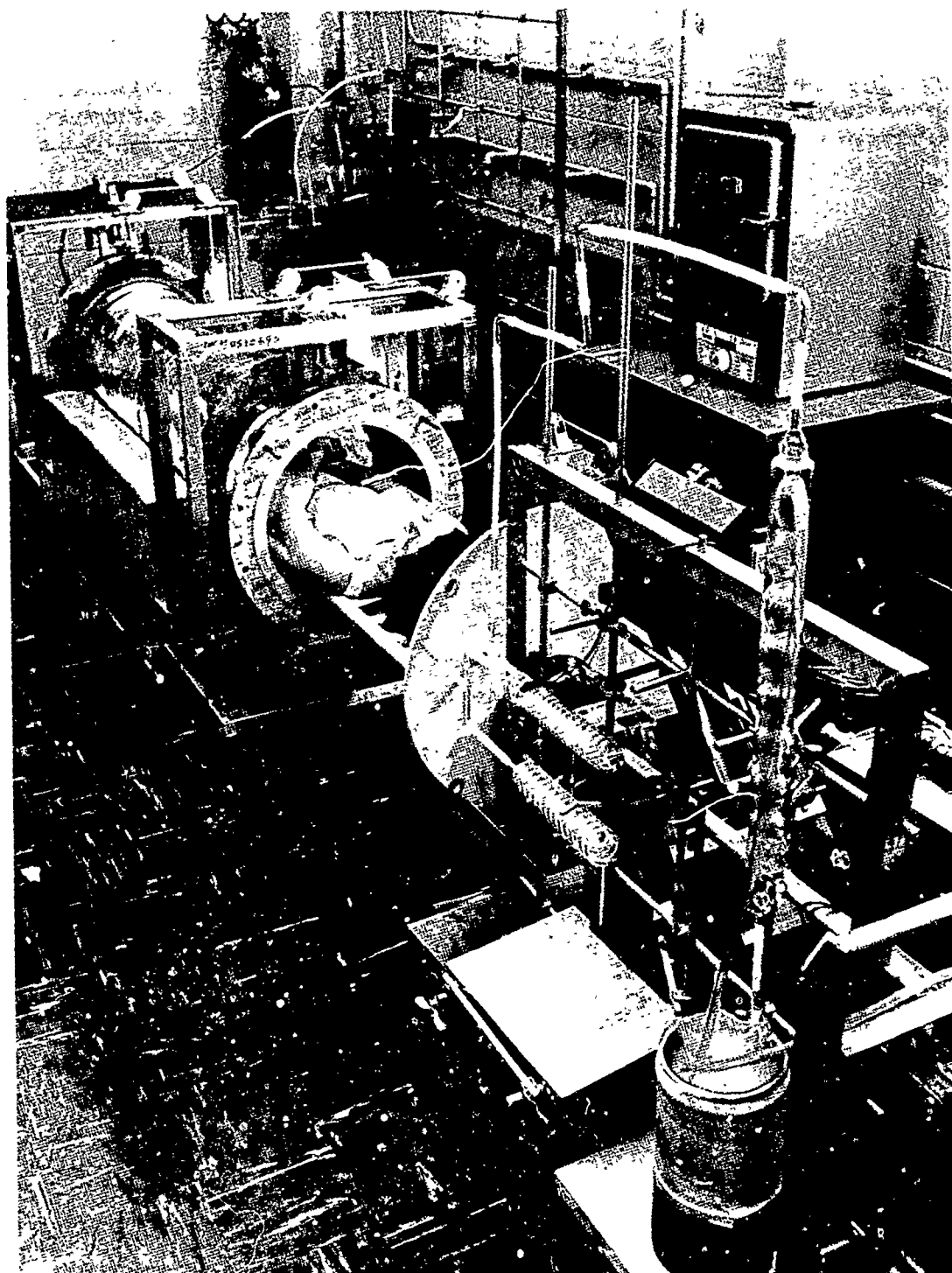


FIGURE 43 - Apparatus for Vapor Collection from Humans

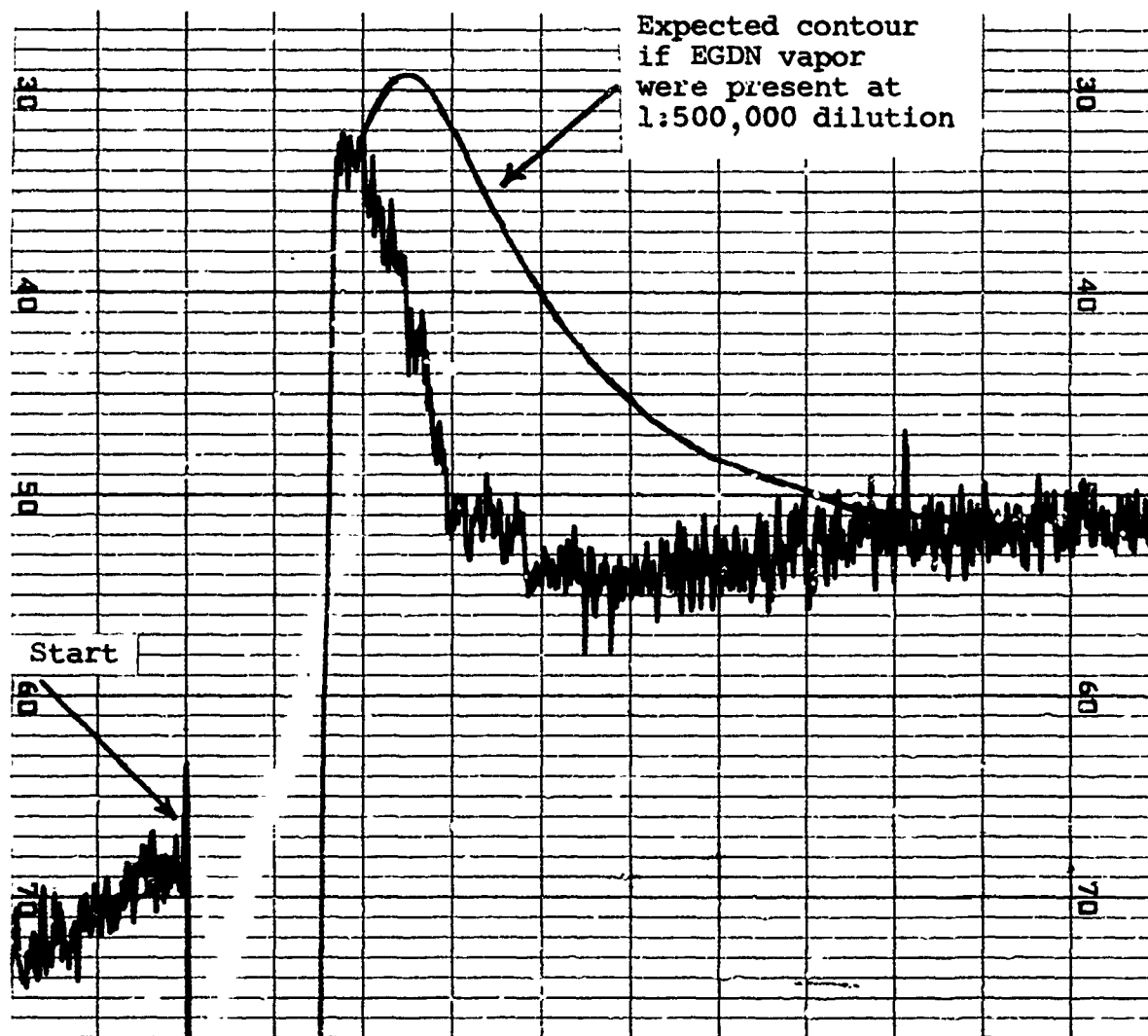


FIGURE 44 - Chromatogram of Vapors from Airborne Human Effluents, Adsorbed on Gold

2.5 Limits of Detection of Accurately Diluted EGDN and Nitrobenzene

Having determined that gold would serve as an efficient trap for EGDN vapors, we planned a series of experiments to determine how diluted vapors can be collected and detected with the gold tube.

For orientation, in Figure 45, the amount of EGDN vapor is plotted versus pressure. This figure is a log-log graph, which allows coordination of linearly related quantities over as many orders of ten as can be seen. The circle on the straight line indicates the vapor pressure of pure EGDN at 25°C. This would normally be the highest possible pressure for EGDN vapors in equilibrium with pure liquid EGDN at 25°C. The source of EGDN was a tube packed with DuPont Gelamite-II.

In our first year's work, mixing EGDN in dynamite was found to reduce the vapor pressure of the EGDN to about 1/5 its normal pressure, apparently as a result of interactions with the other dynamite components. This reduced pressure over dynamite is indicated by the square on the line. It corresponds to a concentration of 0.12 mg/liter and a pressure of 140 μ Hg. Dilutions of a thousand and a million are indicated by the triangle and the diamond, respectively. The corresponding concentrations are 0.12 μ g/liter and 0.12 ng/liter with pressures of 1.4×10^{-5} mm Hg and 1.4×10^{-8} mm Hg.

The following sections describe the experimental procedures and results for dilution experiments.

2.5.1 Experimental Procedures

The gas chromatographic detection system used in this portion of the project is illustrated in Figure 46. The sample injection and partition section consisted of column and detector oven, injection block, column, and carrier gas source.

The column and detector oven was constructed from copper rod, 2 in. in diameter and about 15 in. long, with a hole, large enough to accept the column and the detector, drilled through the rod. The finished rod was wrapped with asbestos paper and Nichrome wire to provide heating. The injection block, which was used primarily for needle injections, was constructed from a 2-in.-OD by 2-in.-long copper block in a similar way.

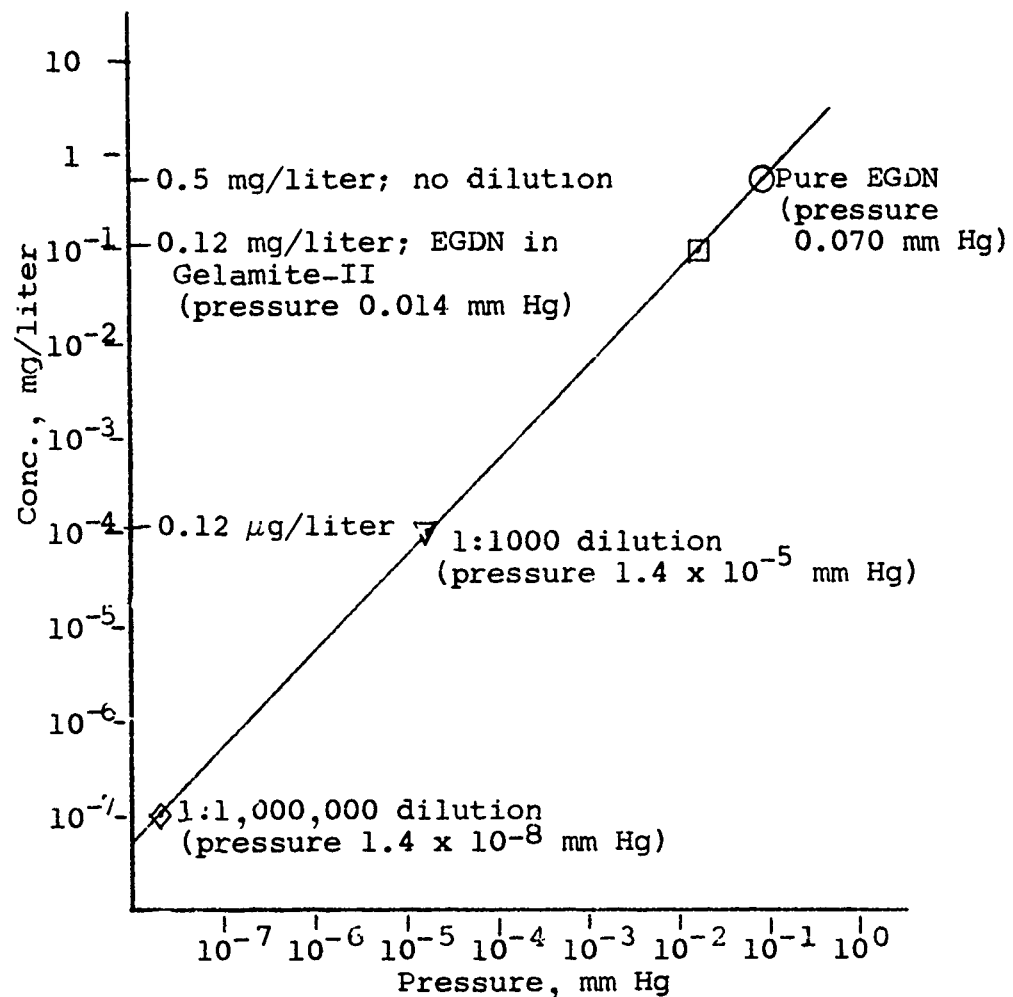


FIGURE 45 - Relation between Concentration and Pressure for EGDN Vapors at 25°C

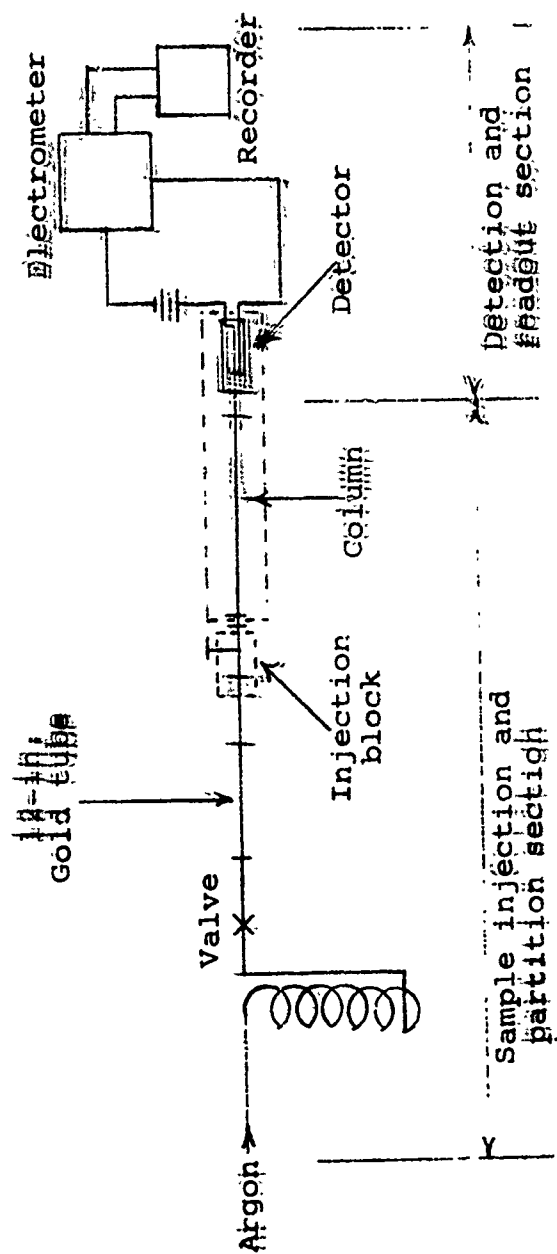


FIGURE 46 - Apparatus for Analysis of EGDN Vapors Adsorbed from Dilution Apparatus

The column was a copper tube, 1/8 in. OD by 1/16 in. OD by 12 in. long, coated with a 10% by weight solution of Carbowax 4000. The carrier gas was high-purity argon. The argon was further cleaned by passing the gas through a trap filled with a Linde type 4A molecular sieve. The molecular sieve was activated at 400°C prior to use. The trap was kept in a Dewar packed with dry ice.

The detection and readout section consisted of the detector, batteries, electrometer, balancing circuit, and recorder. The detector used was the Aerograph Pestilyzer. The batteries gave the 118 v d-c working voltage recommended by earlier experiments. A Victoreen Dynamic Capacitor electrometer, model 475A, provided the signal amplification and measurement. A bucking circuit was used to alter the input. The recorder was a common potentiometric recorder with a 0- to 2-mv range.

EGDN dilutions were obtained by using the continuous flow and mixing apparatus illustrated in Figure 47. Dry bottled air was put through flowmeter A, which monitored the amount of air fed to the EGDN source. The EGDN source consisted of a 1/2-in.-OD by 12-in.-long 316 stainless-steel tube filled with Gelamite-II explosive. The seeded air was diluted by more dry bottled air, controlled by flowmeter B. A portion of this dilution from B was tapped off at flowmeter D, while the rest was discarded. The flow from flowmeter D was further diluted with more dry bottled air, from flowmeter C, to give the desired dilution.

The concentrations of EGDN were calculated as follows.

$$(1) \frac{\text{Flowmeter B (cc/min)}}{\text{Flowmeter A (cc/min)}} = F_1$$

$$(2) \frac{\text{Flowmeter C (cc/min)}}{\text{Flowmeter D (cc/min)}} = F_2$$

$$(3) F_1 \times F_2 = \text{dilution factor.}$$

Example: If flowmeter A is at 20 cc/min, flowmeter B is at 10,000 cc/min, flowmeter C is at 10,000 cc/min, and flowmeter D is at 10 cc/min, then:

$$(1) \frac{1.0 \times 10^4}{2.0 \times 10^1} = 0.5 \times 10^3 = F_1$$

$$(2) \frac{1.0 \times 10^4}{1 \times 10^1} = 1.0 \times 10^3 = F_2$$

$$(3) (0.5 \times 10^3)(1.0 \times 10^3) = 0.5 \times 10^6 = 5 \times 10^5.$$

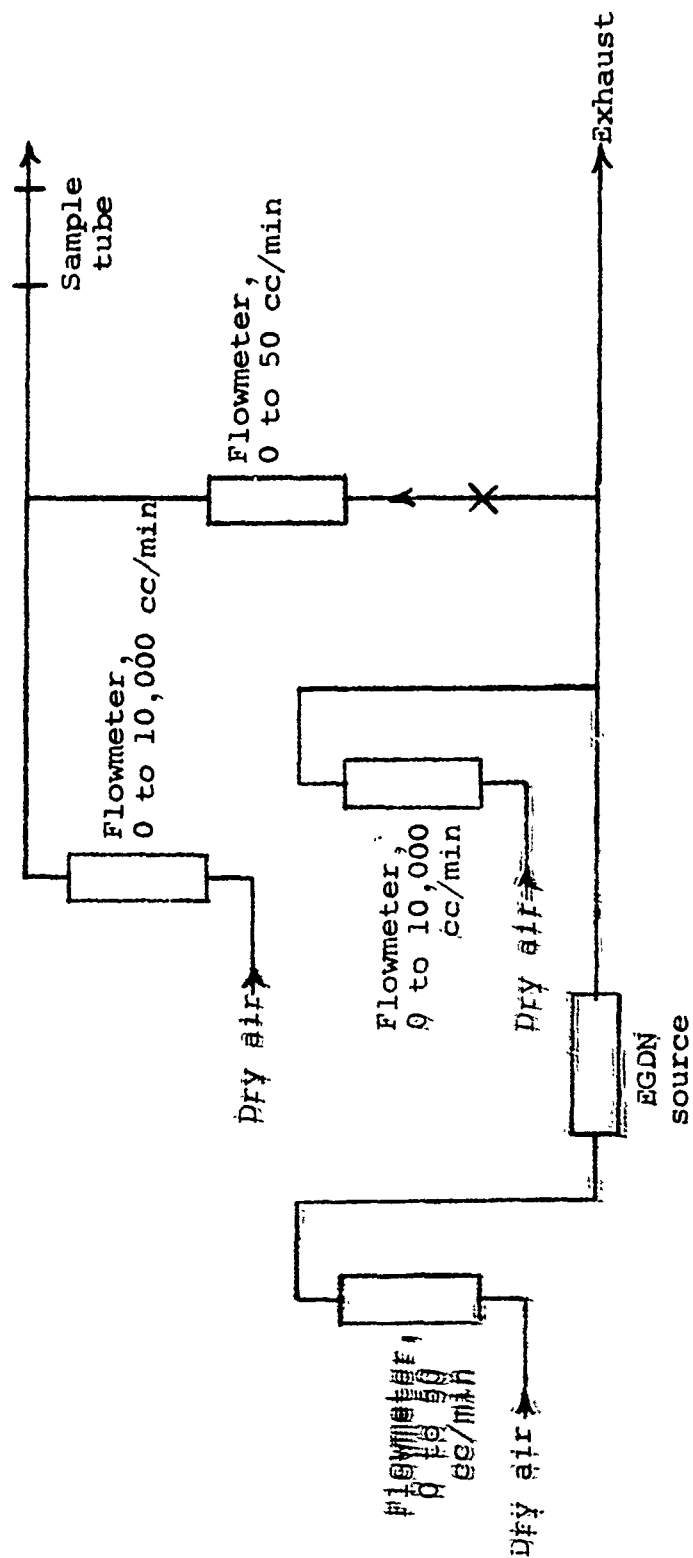


FIGURE 47 - Apparatus for Continuous Dilution of EGDN Vapors with Bottled Air

This gives a dilution factor of 500,000. This means that at the given flow rates, a 500,000:1 dilution was obtained at the sample port. Table IX shows the various dilutions and their respective settings used in the experiments.

TABLE IX - Various Dilutions and Their Respective Settings Used in Conjunction with the Bench Dilution Apparatus

A	Flowmeter, cc/min			D	Dilution
	B	C			
45	10,000	10,000	45		5.0×10^4
25	10,000	10,000	37		1.0×10^5
18	10,000	10,000	37		1.5×10^5
40	10,000	10,000	10		2.25×10^5
20	10,000	10,000	10		5.0×10^5
10	10,000	10,000	10		1.0×10^6
5	10,000	10,000	5		4.0×10^6

2.5.2 Sampling Procedure

In the initial dilution experiments a gold tube 12 in. long, 1/8 in. OD, and 1/16 in. ID was used. It had an interior surface area of 13.8 cm².

A sampling procedure was worked out and adhered to rigidly in order to enable consistent results. The procedure was as follows.

In step 1, the gold tube was inserted into the gas-chromatograph train and heated to 140°C to clean out any contaminants. It was repeatedly heated until the recorder readout indicated that there were no contaminants in the region of interest. The gold tube was finally heated to 80°C to check it out at operating temperature.

In step 2, which was concurrent with step 1, the dilution apparatus was run with the EGDN source disconnected and

plugged. Everything downstream of the EGDN source was cleaned by heating with a heat gun. The cleanliness (absence of detectable EGDN) was checked by taking a sample of the effluent with a clean gold tube. To complete the check, the tube was put in the gas chromatograph and heated to 80°C. If there was any EGDN evident, the gold tube was cleaned as in step 1. If not, and the dilution apparatus was found to be clean, then step 3 was taken.

In step 3, the dilutor was set to the desired dilution and run for 15 min with the EGDN source connected, to equilibrate the system. During equilibration, a dummy tube of Teflon was attached to the dilutor to approximate and maintain the pressure drop and flow conditions that would prevail during sampling with the gold tube. The use of the dummy tube made it possible to saturate the dilutor with EGDN at the desired dilution with a negligible change in concentration when the actual sampling was performed.

The EGDN airflow source was turned off, and the clean gold tube was removed from the gas chromatograph train and put into the sampling port. The EGDN source was then turned back on, and all flows were adjusted to give the desired dilution. The gold tube was exposed to the EGDN-laden air for the desired time, and then step 4 was followed.

In step 4, the gold tube was placed into the gas chromatograph train. After the carrier gas flow leveled out, as indicated by the recorder, the gold tube was heated to 80°C with a heat gun to release the adsorbed EGDN.

Typical conditions used in the experiments were:

Column temp.:	80°C
Injection block temp.:	140°C
Sensitivity:	10×10^{-10} or 3×10^{-10} amp
Argon flow rate:	30 cc/min

2.5.3 Dilution Experiments

2.5.3.1 Clean Air Experiments

Numerous experimental runs were conducted at dilutions from 1:1,000 to 1:1,000,000 using clean dry compressed air. Figure 48 A and B illustrates two of the checks made prior to sampling.

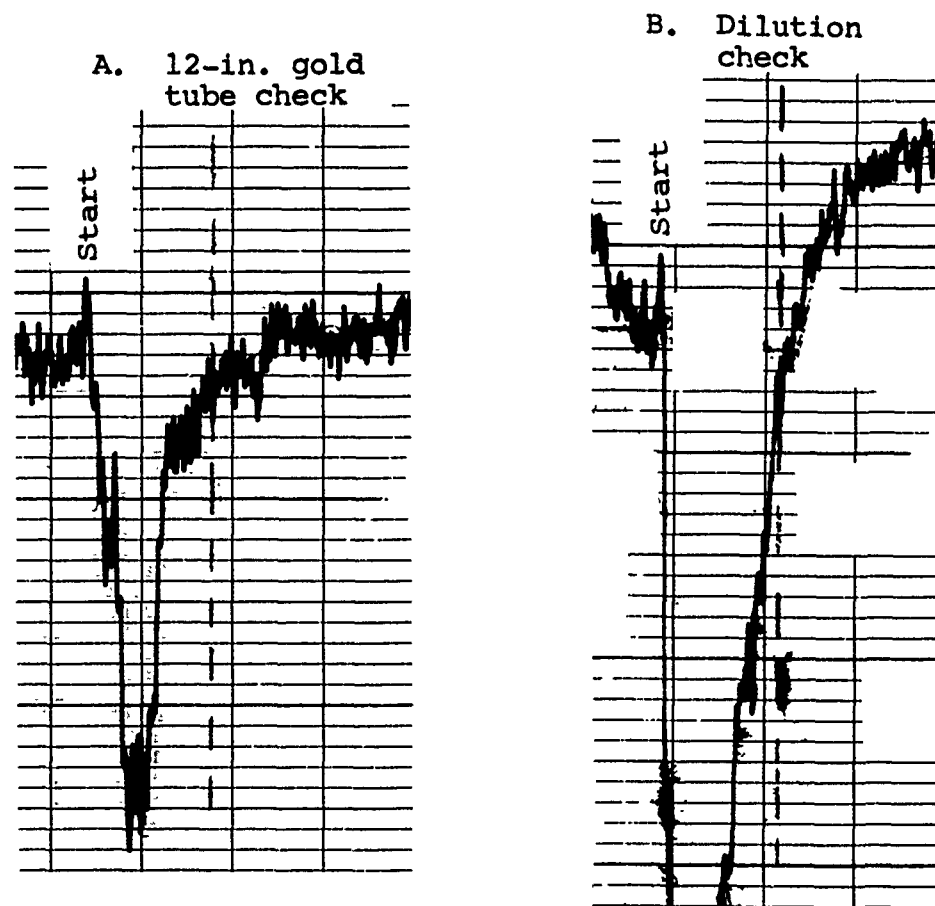


FIGURE 48 - Chromatograms of Clean Apparatus Prior to Sampling of 1:500,000 Dilution of EGDN Vapors

Figure 48A illustrates the recorder response to a clean 12-in. gold tube heated to 80°C. The position labeled as "start" indicates initiation of the heating of the gold tube with the heat gun. As soon as the tube reached the desired temperature, as indicated by a thermocouple affixed to the tube, the heat was turned off. The smooth return to the base line shows that no significant amount of EGDN was adsorbed on the gold tube. The dotted line in Figure 48A indicates the region where EGDN would be expected to appear.

Figure 48B illustrates the recorder response to a clean dilution apparatus. The EGDN source was disconnected and plugged, and the system was continuously flushed with dry bottled air and was heated to 140°C with a heat gun. After the system cooled to room temperature, a clean gold tube was attached to the sample port and a sample of the air was taken for 5 min at a flow of 10 liters/min.

The gold tube was subjected to the treatment outlined in the preceding section. In Figure 48B the smooth return from the negative region indicates that no significant amount of EGDN was present. The dotted line is the portion of the chart where EGDN would be expected to appear.

Figure 49 shows a typical EGDN peak at a dilution of 1:500,000. The sample was released from a 12-in. gold tube that was exposed to the 1:500,000 concentration of EGDN. The sample was collected in 5 min and was desorbed from the gold tube at 80°C. The column temperature was 80°C, and the carrier gas flow rate was 30 cc/min. The instrument sensitivity was 10×10^{-10} amp, and the standing current was 1.94×10^{-9} amp.

Figure 50 shows a typical EGDN peak at a dilution of 1:1,000,000. The 12-in. gold tube was seeded for 5 min with the diluted EGDN, which was released by heating to 80°C. The column temperature was 80°C, and the carrier gas flow was 30 cc/min. The sensitivity and the standing current were the same as before. Higher dilutions (1:4,000,000) were used, but no definite trace of EGDN was detected.

2.5.3.2 Effect of Collection Time

The amount of EGDN collected should depend on the length of time the diluted vapors are passed through the tube. In a series of experiments similar to those described above, diluted vapors were passed through the gold tube for various periods of time. Usually, 5 sec, 30 sec, 1 min, and 5 min were used. The flow rate was 10 liters/min.

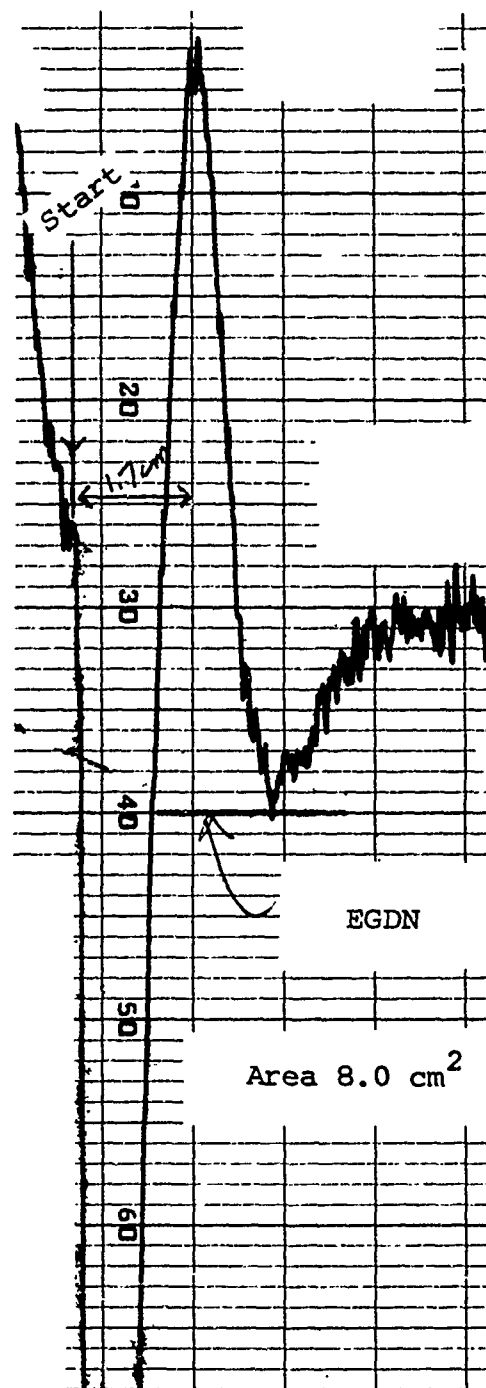


FIGURE 49 - Chromatogram of 1:500,000 Dilution of EGDN Vapors
Collected by 12-In. Gold Tube

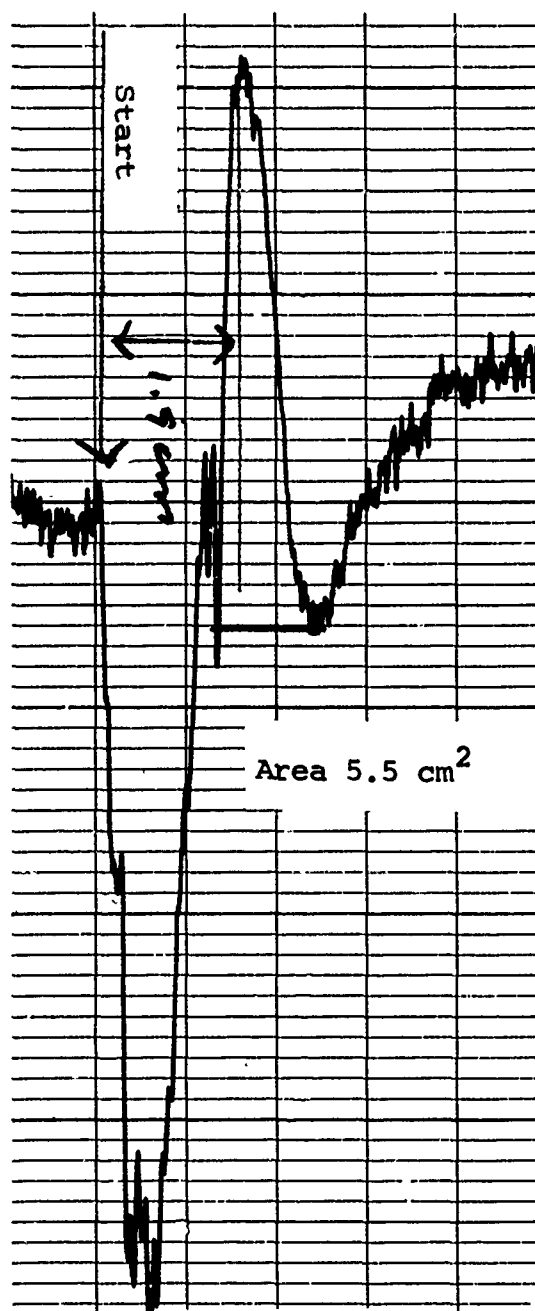


FIGURE 50 - Chromatogram of 1:1,000,000 Dilution of EGDN Vapors
Collected by 12-In. Gold Tube

The data collected are plotted in Figure 51. The amount adsorbed was calculated from the area under the EGDN traces by using the approximate factor $1 \text{ cm}^2 = 1 \text{ ng}$ of EGDN. To get this factor the gain settings for the electrometer were 1A on the attenuator and 3×10^{-9} amp full scale on the sensitivity selector. When using other electrometer settings, the above factor has to be adjusted to account for the change in amplification involved. This has been already done for these data.

Several interesting facts can be deduced from Figure 51. For each dilution, the amount adsorbed reached almost its maximum in about 1 min of flow time. Hence it is not necessary to pump air through this type of trap for an extended period of time. This is a self-limiting collection system that rapidly becomes equilibrated with dilute vapor and does not accept more vapor. These extra vapors simply pass on through.

Note also that a change from a dilution of 1,000 to 1,000,000 (a ratio of 1000:1) changes the amount collected in 5 min by a factor of only about 20:1. This effect is inherent in the nature of adsorption isotherms involved in the collection process. As the pressure or concentration of EGDN is reduced, there are fewer molecules to be adsorbed, but the ones adsorbed are held more strongly. Hence, nonlinear effects (discussed in Section 2.4 on adsorption) operate to improve the overall effectiveness of the system.

2.5.3.3 Contaminated Air Experiments

Dilution experiments were performed with room air in order to ascertain the effect of possible background contaminants present in room air. These could shroud the EGDN peak on the recorder.

The dilution apparatus used was essentially the same, with changes as follows. (1) The dry air tanks were disconnected, and the lines were left open to room air, as shown in Figure 52. These were the air inlets. (2) Vacuum pumps were installed along with small ballast tanks, as shown in Figure 52. These were used to provide airflow through the dilutor system.

The dilution determination, transfer, and sampling steps were the same as before. Because of the limited pump capacity, dilutions no higher than 1:500,000 were obtained. Most dilutions were between 225,000 and 500,000.

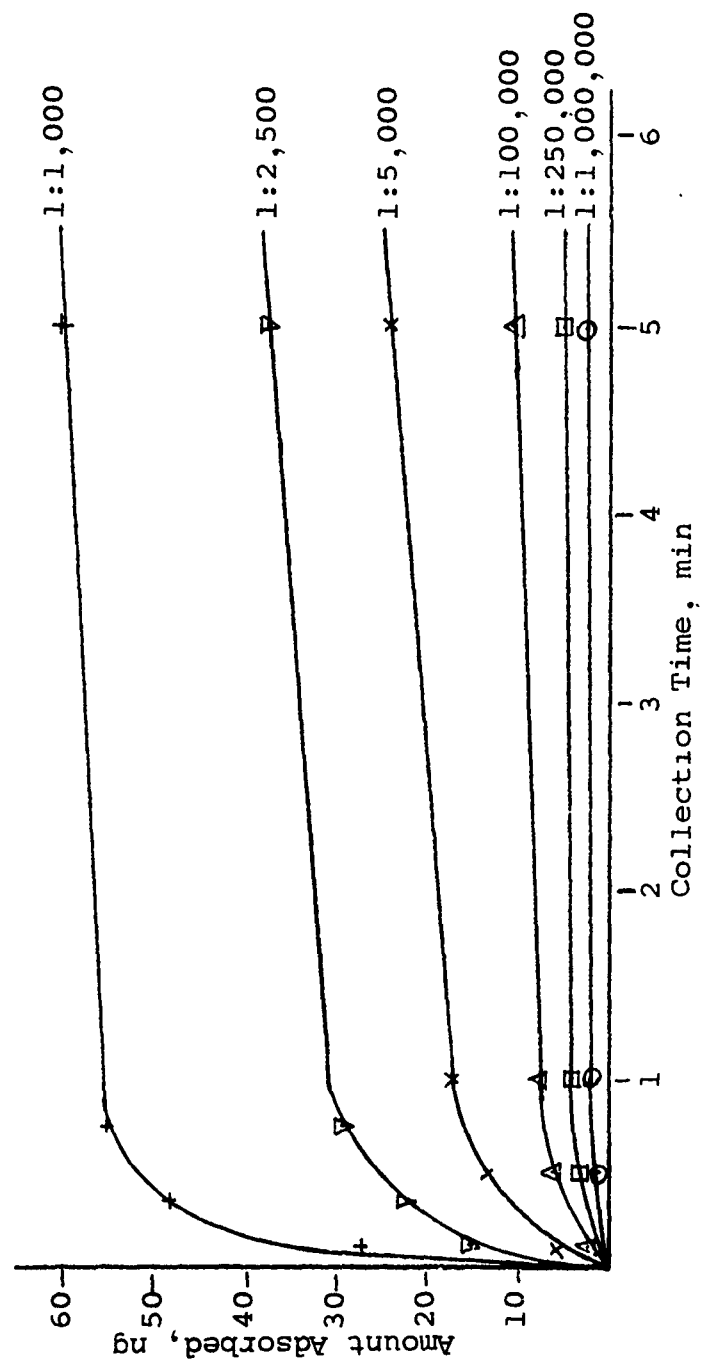


FIGURE 51 - Adsorption of Various Dilutions of EGDN on a Gold Tube versus Duration of Sampling

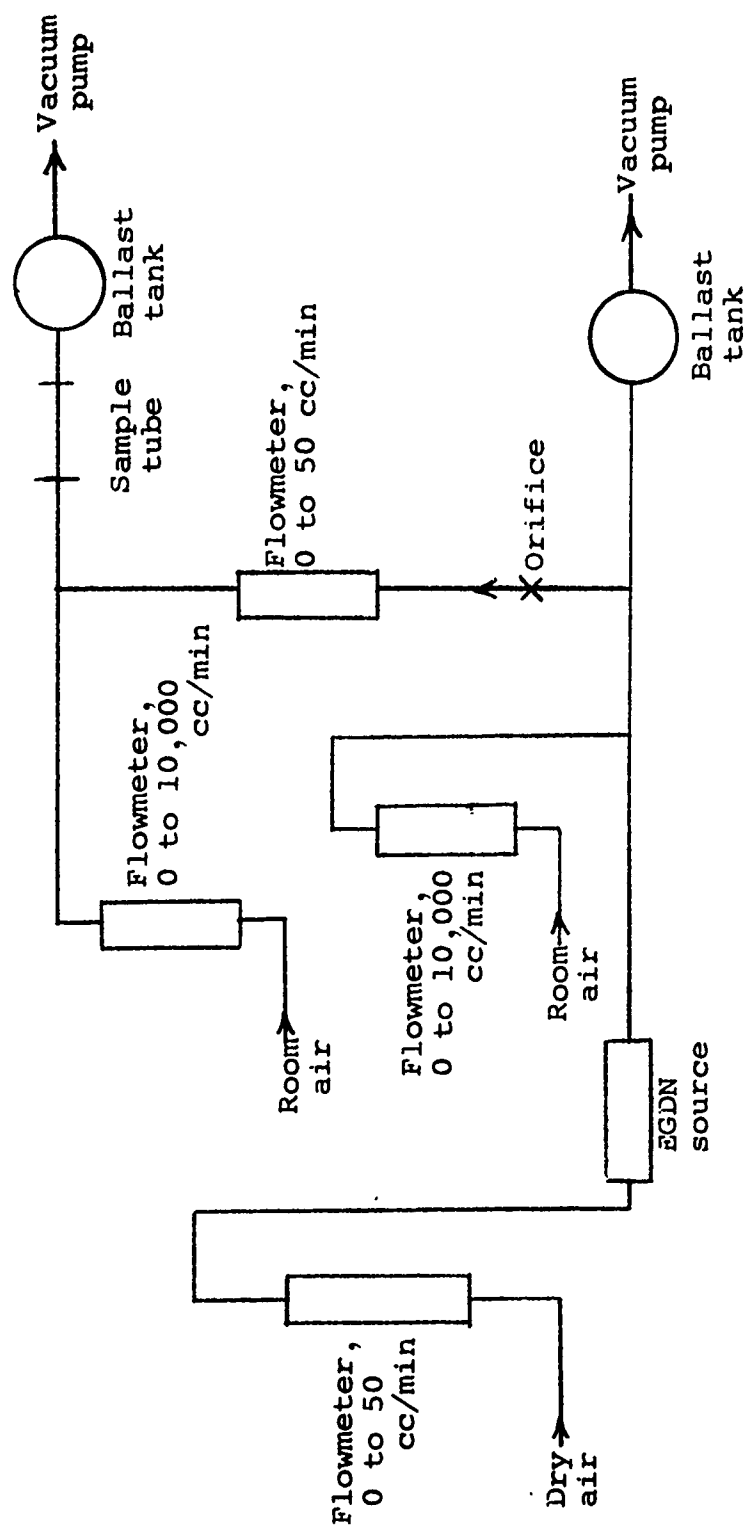


FIGURE 52 - Apparatus for Continuous Dilution of EGDN Vapors with Room Air

Background contaminants did not seem to be a hindrance. Any contaminants that were detected fell into two categories. The types of contamination are illustrated in Figure 53. The first category consisted of volatile substances that were retained approximately the same amount of time as the EGDN. These were in such low concentrations that they proved to be of no consequence. The EGDN peak was large enough in proportion to the portion of the background to be easily distinguished. The second category consisted mainly of heavier, less volatile compounds, which had a much longer retention time than the EGDN.

Nitrobenzene on a Carbowax 4000 column shows a retention time not too different from that of EGDN and also produces a response in the electron-capture detector. Therefore, several experiments were performed on nitrobenzene retention characteristics on gold at high dilutions, to determine whether nitrobenzene adsorbs during the EGDN collection step and whether it desorbs at 80°C.

The bench dilution apparatus was reconnected to the dry bottled air, and the EGDN source was exchanged for a nitrobenzene source. The nitrobenzene source consisted of a piece of 316 stainless-steel tubing 5 in. long and 1/2 in. OD. The interior was packed with glass wool with 4 drops of nitrobenzene deposited on it. The dilution, transfer, and sampling techniques used were the same as before.

The experiments were performed at dilutions of 500,000 and 1,000,000. Figure 54 shows the nitrobenzene peak at a dilution of 1:1,000,000. The nitrobenzene peak is in the position where it interferes with the EGDN peak (compare Figure 50). Figure 54 illustrates that nitrobenzene is adsorbed on gold with EGDN and desorbs together with EGDN at 80°C. Thus, in columns with Carbowax coating, nitrobenzene even at high dilutions can be a harmful contaminant if not properly retained by the column phase. Subsequently, an Apiezon-L-on-Fluoropak column was found to solve this problem, since the EGDN emerged well in advance of nitrobenzene.

2.5.4 Short-Tube Experiments

It was observed in the previous experiments that the peaks traced out on the recorder paper, although relatively easy to detect, were not very sharp and were too broad. Previous experience indicated that the sharpness and the breadth of the peak very often are related to the length of time needed for the complete sample to travel through the detector.

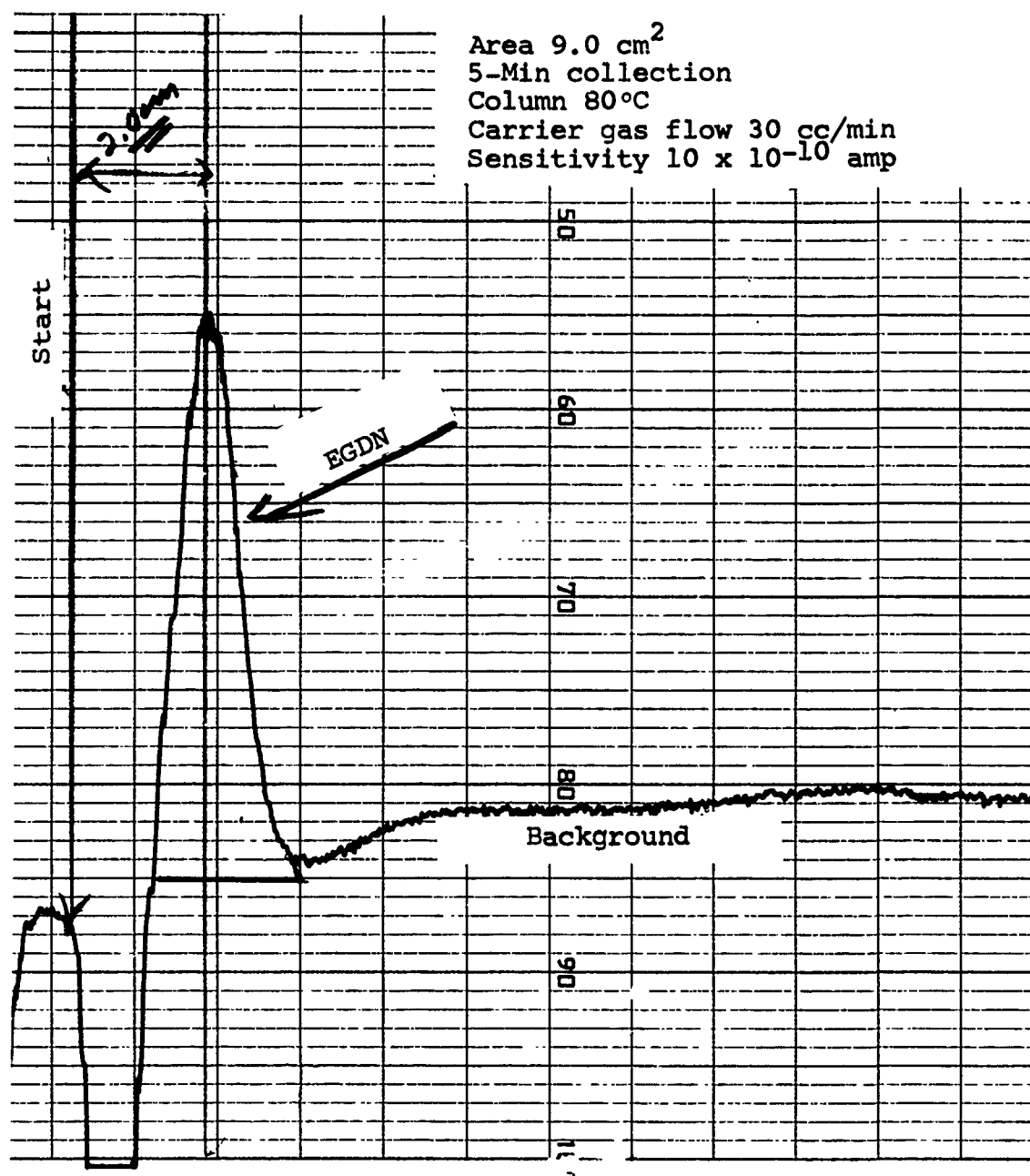


FIGURE 53 - Chromatogram of EGDN Vapors Diluted 1:225,000
with Room Air

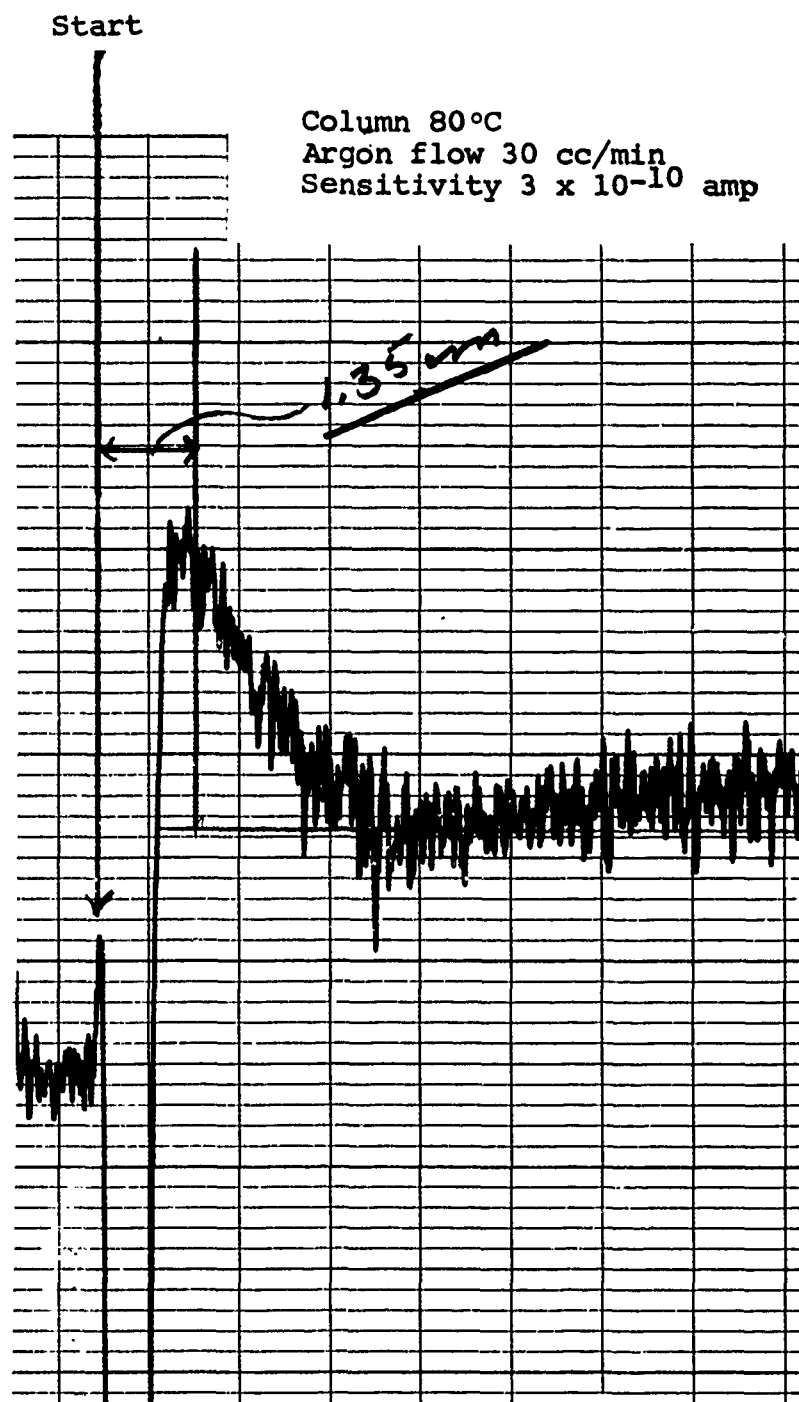


FIGURE 54 - Chromatogram of Nitrobenzene Vapors
Diluted 1:1,000,000 with Room Air

In other words, the faster the sample travels through the detector, the less broad the peak traced on the recorder paper. As a result, the slope of the tracing is greater and thus gives a sharper peak. Heating of the long tube was uneven, and so the sample was released from the gold surface unevenly. It was believed that a shorter gold tube with an insulating oven-like box around it would solve this problem. A 3-in. gold tube with a 1/8-in. OD, a 1/16-in. ID, and an inner adsorptive area of 3.7 cm² tube was used in a series of comparative experiments. The conditions of the experiments were essentially the same as before. The bench dilution apparatus was used, with dry bottled air, and the column detector systems were the same as before. The dilutions ranged from 500,000 to 4,000,000.

As expected, there was a pronounced increase in peak sharpness and a decrease in peak breadth. There was also an expected retention-time decrease, which was desirable. A peak obtained from the 3-in. tube at a dilution of 1:1,000,000 is shown in Figure 55, which should be compared with Figure 50 to illustrate these points.

Another result was an increase in EGDN detection capability. With the 12-in. gold tube, the maximum dilution at which EGDN could be definitely detected was 1:1,000,000. With the 3-in. gold tube, EGDN was repeatedly detected at a dilution of 4,000,000. This increase was due to a rapid release of EGDN when the 3-in. gold tube was heated.

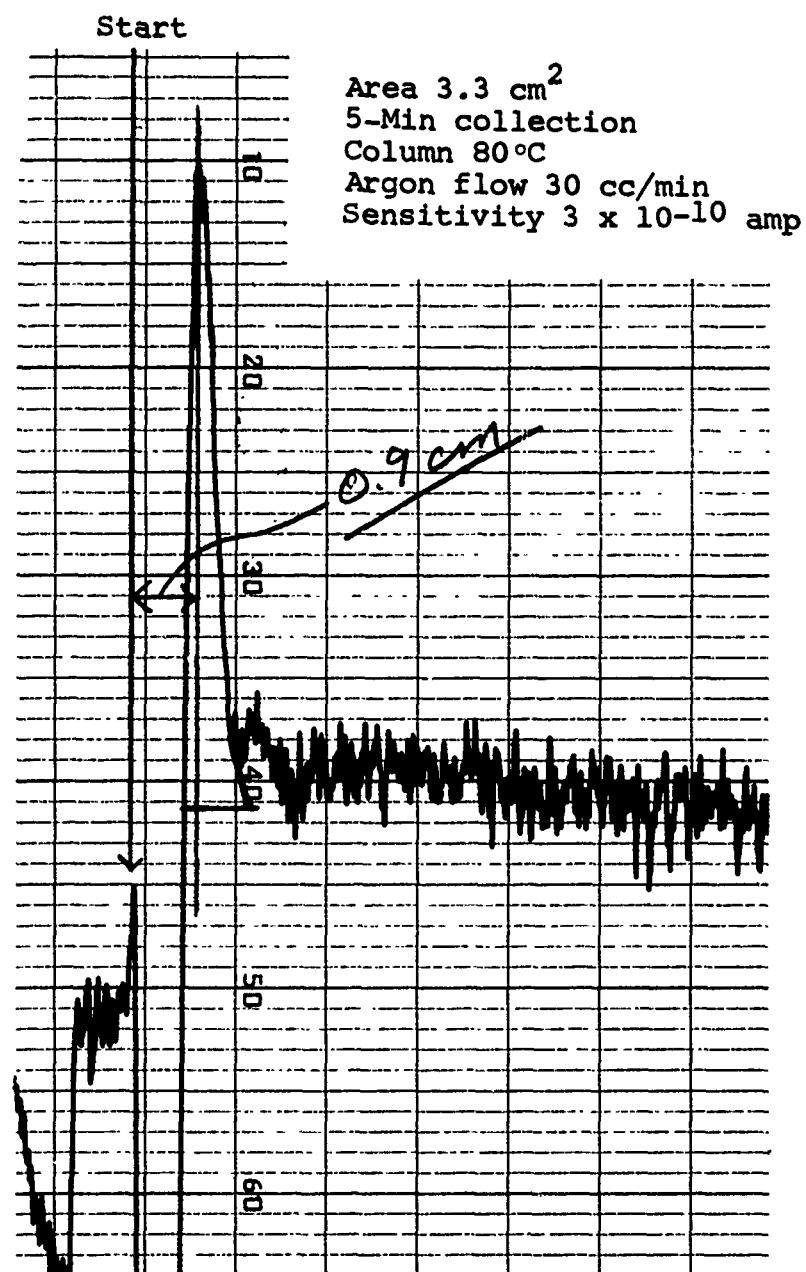


FIGURE 55 - Chromatogram of EGDN Vapors Collected by 3-In. Gold Tube

3.0 INVESTIGATION OF OTHER DETECTORS

In addition to the electron-capture detector, two other possible detection techniques that recently have been developed appeared to merit further study. These were microwave absorption spectrometry and microwave-heated argon-plasma emission spectrometry. The first, in principle, can provide an extremely characteristic line pattern for each different molecular species and thus serve as a unique fingerprint of EGDN or other vapors associated with explosives. The second is not as specific, except to compositional component atoms (C, H, N, O, and S), but is extremely sensitive, especially for compounds that contain carbon and nitrogen. It has been claimed also to detect 10^{-9} g of sulfur compounds, and thus matches the sensitivity level the electron-capture detector possesses for EGDN.

The potential usefulness of these detector techniques was explored on vapors of EGDN and some other compounds. Since black powder was among explosives of interest in connection with bomb detection and its vapor was not detectable by techniques based on electron-capture detection, the microwave-heated argon-plasma technique was tried on black powder vapors. Additional tests, by the conventional hydrogen-flame ionization detector, were conducted on amounts and composition of organic vapors from black powder.

3.1 Microwave Absorption Detector

To improve the selectivity and the sensitivity of the bomb-vapor detection system, vapors from typical explosives were studied by microwave spectrometry. The study was made under the auspices of the Hewlett-Packard Co., at their microwave research laboratory in Palo Alto, Calif., from June 1 through June 11, 1965. The use of their laboratory and the cooperation of Mr. Stuart Armstrong and others of the Hewlett-Packard Co. in collecting bomb vapor samples and operating the spectrometer are gratefully acknowledged.

3.1.1 Principles

The instrument used was the model 8400A microwave spectrometer shown in Figure 56. This instrument electronically generates microwave power at a level of 20 mw in the range 8.2×10^9 to 12.4×10^9 cps, known as the X-band.

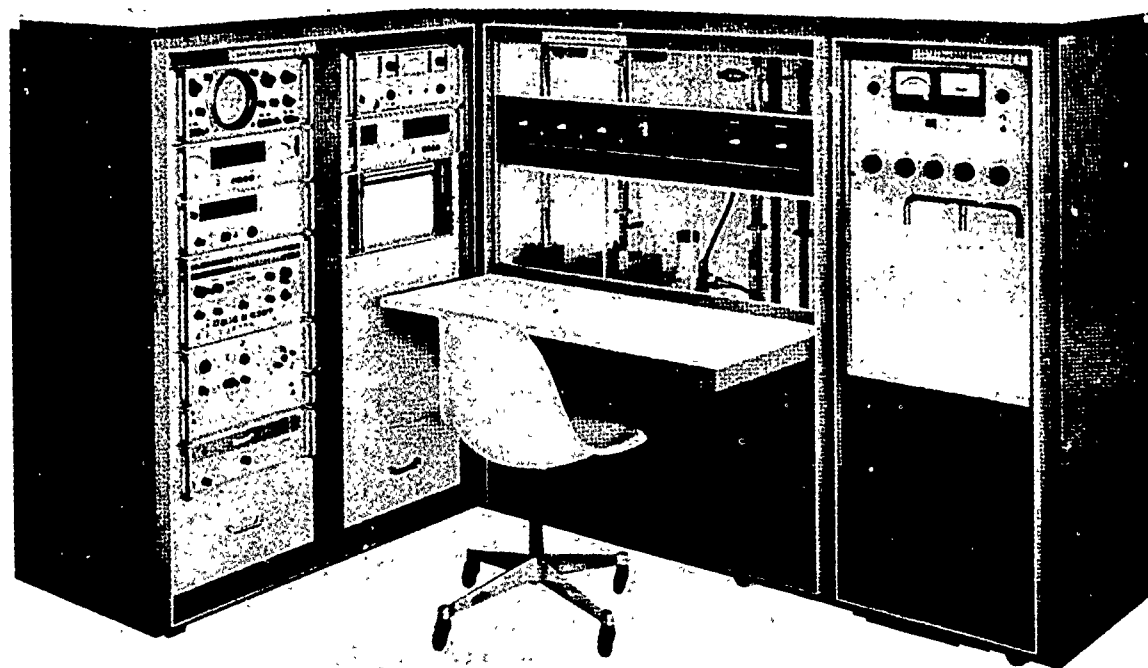


FIGURE 56 - Model 8400A Microwave Spectrometer
(Hewlett-Packard)

This power is fed to two arms of a balanced bridge network of waveguide tubing. One arm of the bridge contains the vapors to be examined. When the vapors absorb microwave energy, the bridge becomes unbalanced. This unbalance is detected, amplified, and recorded on a strip chart. The recorder chart is calibrated by a signal from the microwave source. This signal causes an auxiliary pen on the recorder to make a blip every 100 mc/sec as the source sweeps through the X-band.

When an electromagnetic wave in the microwave region acts upon a polar molecule,* the oscillating electrical field induces rotation of the molecular dipole. The rotational energy can be accepted by the molecule only in discrete quantities, $\Delta\epsilon$, depending on the momentum of inertia of the molecule around the axis of its rotation.

For a simple molecule with one momentum of inertia

$$\Delta\epsilon = \frac{h^2}{8\pi^2} \frac{J(J+1)}{I}$$

where h is Planck's constant, I is the appropriate momentum of inertia, and J is any integer, The value of the rotational quantum, $\Delta\epsilon$, is connected to the frequency of the impinging electromagnetic wave through

$$\nu = \frac{\Delta\epsilon}{h}$$

Thus, the energy of the microwave is absorbed by the molecule only if certain characteristic values of frequency are used. Also, a sufficient number of intermolecular collisions must occur between the molecules in the vapor, so that the rotationally excited molecules can lose their energy and be prepared for repeated absorption of the energy from the microwave. Usually, the most desirable pressure in the microwave cell is 1 to 100 μ .

* Polar molecules are those in which the center of all negative charges (electrons) does not coincide with the center of all positive charges (atomic nuclei), but there is no overall net charge. For example, in water the configuration is $\text{H}-\text{O}-\text{H}$ and the negative charges are located in the vicinity of oxygen, but the positive charges are closer to the line drawn from H to H.

The characteristic absorption frequencies in the microwave range thus describe principally the property of the polar molecules as a whole. This contrasts with infrared absorption and Raman scattering, which characterize principally the properties of parts of molecules (bonds, functional groups) and the visible and ultraviolet spectra that describe the electronic transitions within the molecule.

Microwave absorption peaks are sharp, and the possibility of the coincidence of having almost the same absorption frequencies for different molecules is small. High resolution is instrumentally possible. Small polar molecules consisting of a few atoms have characteristic microwave frequencies in the range of 10^{10} to 11^{11} cps. Smaller molecules, such as water, absorb at high frequencies outside the above range. Large polyatomic molecules absorb at lower frequencies.

The microwave technique offers positive identification of chemical species. After the exact position of the peak has been determined, simple circuitry specializing on this specific frequency can be used and low-level signals can be distinguished. The microwave absorption varies with the partial pressures of the polar component and other gases present. With a decrease in concentration and total partial pressure, the peak narrows and finally disappears by becoming too narrow. At higher partial pressures, the molecules undergo the Stark effect - splitting in the electrostatic field produced by other molecules -- and the peaks broaden diffusely. For optimum detection, the pressure in the absorption cell must be kept within a specified range.

3.1.2 Experimental Procedures

The Stark cell of the model 8400A spectrometer has a volume of about 250 cc and requires about 100μ Hg pressure for best operation. To deliver vapors to the Stark cell, several milligrams of explosive vapors were collected into a sampling tube to provide saturation vapor pressure in the cell. This amount can easily be seen on the walls of the sampling tube.

For collection of vapors from complex explosives, about 100 g of powdered explosive was placed in a 1-in.-OD Pyrex tube about 6 in. long with an 8-mm-OD outlet as shown in Figure 57. Helium gas from a tank, H, was reduced to low pressure by a gage, G, and passed through a needle valve, N, for fine control. The helium then passed through a clean copper tube and through a rubber stopper, R, and on over the

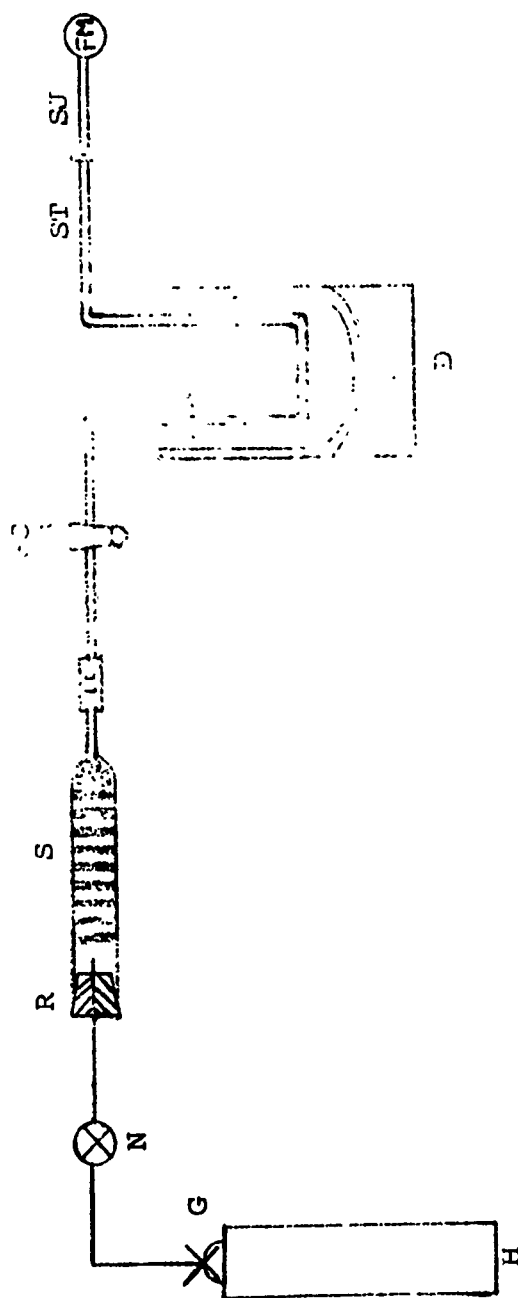


FIGURE 57 - System for Collection of Explosive Vapors

powdered sample, S, to a U-shaped sampling tube, ST, fitted with a stopcock, SC, and a 14/35 standard taper joint, SJ, for attachment to the spectrometer vacuum system. The depleted helium was then led to a soap-bubble flowmeter, FM, to measure the flow rate. The Dewar, D, was supplied with dry ice-acetone, melting carbon tetrachloride, or ice water, as required by the various samples. Generally, 2 to 4 hr was required to collect noticeable amounts of liquid EGDN in the sampling tube.

For pure chemicals such as di- and trinitrotoluene, small amounts were placed into a sampling tube connected directly to the microwave spectrometer vacuum system.

Samples from complex mixtures such as Gelamite-II, smokeless powder, and nitroglycerine tablets released about 1 cc of liquid. Small droplets of another liquid floated on the surface of the predominant phase. Since nitroglycerine and nitroglycol are insoluble in water, it was assumed that the bulk of the liquid collected was water, with condensed explosive vapors floating on it and attached to the walls of the tube.

Since water has a vapor pressure of 25 mm Hg at room temperature, or a vapor pressure about 250 times greater than desirable in the Stark cell, the water had to be removed. This was done by adding 1 cc of pure benzene to the sampling tube to dissolve the explosive vapors but not the water. The benzene phase was then transferred to another sampling tube. Benzene was chosen as the solvent because it has a high vapor pressure, is a good solvent for EGDN, etc., and has no known microwave spectral lines in the X-band.

Because of the high vapor pressure of benzene relative to the explosive vapors, its excess was readily removed by pumping vapors from the solution, which was cooled to -22°C with melting carbon tetrachloride in the Dewar. The bulk of the benzene was removed in 15 to 20 min, and a thin layer of droplets of explosive vapors remained on the walls of the sampling tube.

As will be seen in the following section, it was not possible to remove acetone from the vapors by this technique, even though acetone has a higher vapor pressure than benzene. Also, acetone has many strong absorptions in the X-band, and the slightest amount (perhaps less than $1\ \mu\text{ Hg}$ pressure) produces the entire acetone spectrum.

3.1.3 Experiments

Tables X and XI give data on the sample collection experiments and microwave measurements, respectively. The explosives used were described in detail in Federal Aviation Agency Technical Report FAA-ADS-34, page 8. They represent typical high-explosive substances and mixtures used for construction and mining operations and in 1- or 2-lb quantities are adequate for in-flight destruction of aircraft.

In sample 2-15-1, the vapor sample was placed directly on the spectrometer and pumped at 0°C to remove the water. The amount of sample was not large and consisted mainly of water. Consequently, pumping at 0°C was too drastic, and the entire sample disappeared.

By extending the collection period to 8 hr (sample 2-17-1) and extracting with benzene, it was possible to get enough nitroglycol and nitroglycerine to get a pressure of 180 μ Hg in the vacuum system. This is the approximate vapor pressure of nitroglycol at room temperature.

Sample 2-17-1 was run on the spectrometer under the conditions listed under run 25 in Table XI. The pressure was 70 μ Hg in the Stark cell during the run. This was obtained by bleeding in vapors from the sample volume to the previously evacuated Stark cell. The pressure decreased momentarily during this operation but returned to 180 μ Hg again. Visible droplets of liquid remained on the sampling tube. Thus, more than enough material was available to fill the Stark cell and it behaved like a pure substance. For this reason we concluded that acetone was present in very low concentration and yet was readily observed in the spectrum of this sample.

The microwave power used is the rate at which electromagnetic energy at a frequency in the range of 8,200 to 12,400 mc/sec passes down the Stark cell when no absorption by vapor takes place. Since the bandwidth of the waves is only a few kilocycles, the frequency and the absorption can be measured with great precision. The Stark voltage is the d-c voltage applied between the walls of the waveguide and a central metallic strip insulated from the walls.

The attenuation is a measure of the amount of unbalanced power reaching the crystal detector. Great attenuation means less noise but also lower signals. For pure acetone (run 27A), the absorption intensities were so strong that an attenuation of 30 db was found to be suitable, whereas for nitroglycerine (run 29), 20 db was suitable.

TABLE X - Summary of Collection Experiments

Sample	Material	Helium Flow, cc/min	Time, hr	Volume, cc	Temp. of Sample, °C	Remarks
2-15-1	DuPont Gelamite-II	1.0	2	0.2	25	Pumped on sample at 0°C. Entire sample disappeared. No spectrum taken.
2-17-1	DuPont Gelamite-II	1.0	8	0.5	25	Extracted with benzene. Purified at -22°C by vacuum pumping. Spectrum taken.
2-22-1	Nitroglycerine tablets	1.0	12	1.0	68	Heated sample to hasten collection. Extracted with benzene. Purified in vacuum at 0°C. Spectrum taken.
2-25-1	Smokeless powder	1.0	4.5	0.1	25	Sample too small to work up. Discarded.
2-25-2	Smokeless powder	1.0	3.0	1.0	70	Heated sample to hasten collection. Extracted with benzene. Purified in vacuum at -22°C.

TABLE XI - Summary of Microwave Experiments

Run	Sample	Pressure, mm. Hg	Microwave Power, mw	Voltage, V d-c	Attenuation, db	Time Constant, sec	Sweep Rate, 2 kc/sec	Chart Speed, ipm	Remarks
23	ortho-Nitrotoluene	70	10	600	26	1	350	0.5	Pure liquid was contaminated by acetone. No peaks from ortho-nitrotoluene.
24	Dinitrotoluene	25	10	580	28	1	350	0.5	Vapor from solid. No microwave absorption.
25	2-17-1 ^a (from Gelamite-II)	70	10	500	26	1	350	0.5	Many peaks. Some from acetone.
27A	Acetone	60	10	600	30	1	350	0.2	Pure acetone vapors.
27B	ortho-Nitrotoluene	112	10	580	22	1	350	0.5	Contaminated by acetone and Gelamite. No new peaks.
29	2-22-1 ^a (from nitroglycerine tablets)	65	10	520	20	1	350	0.2	Sample gave only 12 μ pressure. Air added to get 65 μ total pressure. Acetone present.
31	Trinitrotoluene	65	10	500	22	3	150	0.2	Pure trinitrotoluene powder. No microwave absorption.
32	2-25-2 ^a (from smokeless powder)	60	10	500	24	3	150	0.2	Spectrum very similar to Gelamite. Acetone present.

^aSee Table X.

The time constant and the sweep rate relate to the rate at which the microwave source sweeps through the X-band. Generally, the sweep was 350 kc/sec^2 . Thus a run from 8.2×10^6 to $12.4 \times 10^6 \text{ kc/sec}$ required 12,000 sec, or about 4 1/2 hr.

3.1.4 Results and Discussion

In general, the data show that materials containing nitroglycerine and nitroglycol give numerous distinct microwave absorption peaks in the X-band, while substances like trinitrotoluene do not.

Figure 58 is a reproduction of the spectra of acetone and Gelamite-II vapors; the acetone peaks have been deleted in the Gelamite spectrum. The Gelamite sample was contaminated by acetone, as were the samples from nitroglycerine and smokeless powder. Table XII is a list of the frequencies and the relative intensities of the Gelamite peaks. The absolute intensity of these peaks is about $10^{-8}/\text{cm}$ in terms of the usual definition of the microwave absorption coefficient. Lines of $10^{-6}/\text{cm}$ are considered very strong, $10^{-8}/\text{cm}$ medium, and $10^{-10}/\text{cm}$ very weak. Hence, the lines observed in the Gelamite-II, nitroglycerine tablet, and smokeless powder vapors are of medium intensity and are typical of X-band absorption lines.

Data on nitroglycerine tablet vapors (run 29) and smokeless powder vapors (run 32) are listed in Tables XIII and XIV, respectively. The pure acetone lines obtained in run 27A are listed in Table XV.

For comparison, these data are plotted in Figure 59. The lines are idealized to zero width for clarity. Notice that three lines at 9800 mc/sec appear for Gelamite and smokeless powder but not for nitroglycerine or acetone. This suggests that they are due to EGDN, while the lines from 10,800 to 12,300 are mostly due to nitroglycerine.

Although it is very likely that the above microwave absorption lines are due to EGDN and nitroglycerine, it is not 100% certain. Mr. Stuart Armstrong and others at Hewlett-Packard Co. suggested that a theoretical calculation of the spectra be made based on known bond angles and bond distances for these molecules. Several groups at various universities have written computer programs capable of making such calculations and have had excellent agreement between theory and experiment. Such prediction of absorption lines and relative intensities would prove the above assumption.

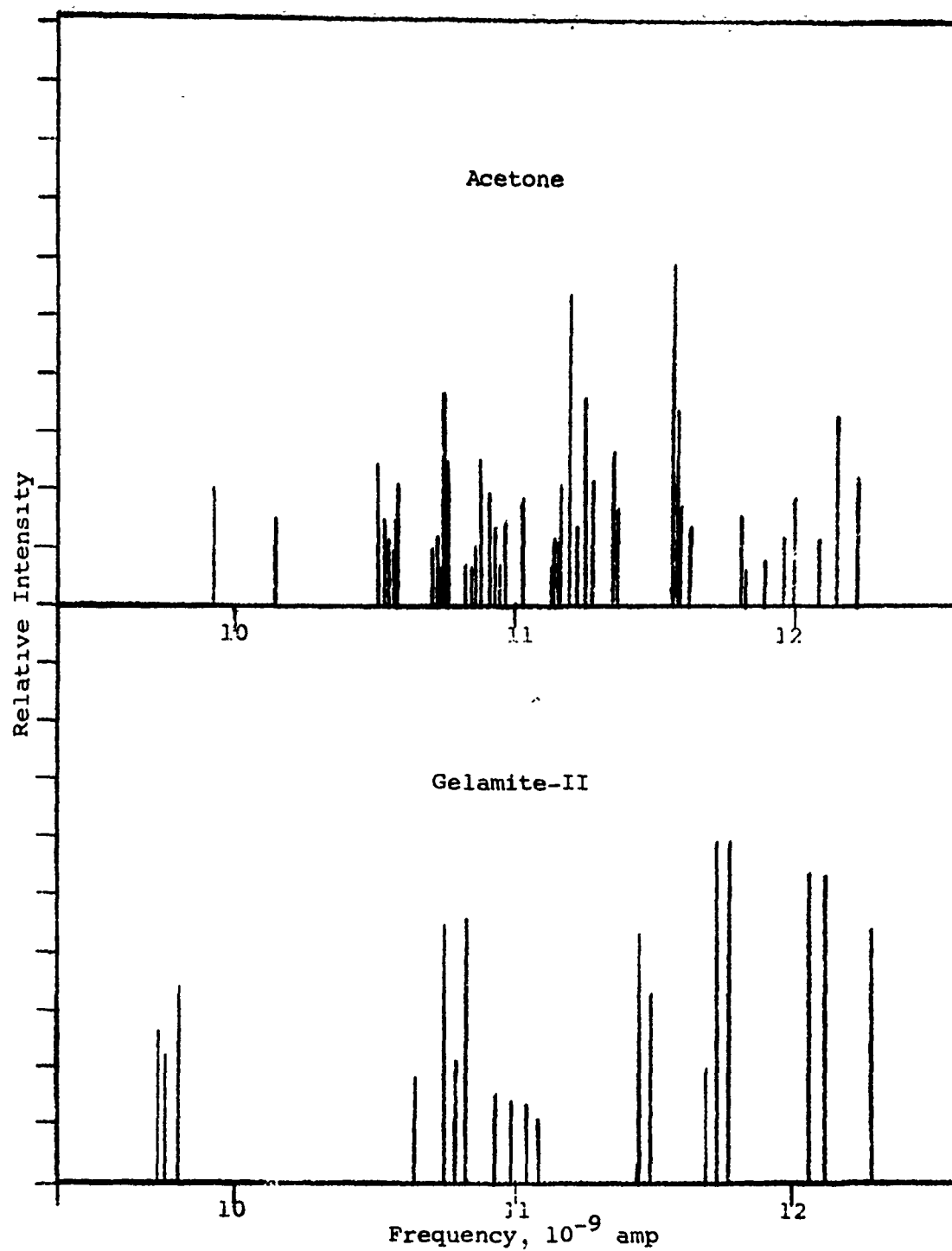


FIGURE 58 - Microwave Spectra of Acetone and Gelamite-II

TABLE XII - Microwave Absorption Frequencies and Relative Intensities Observed in Gelamite-II Vapors (Run 25)

<u>Frequency, mc/sec</u>	<u>Intensity, arbitrary units</u>
9751.9	27
9777.2	23
9826.7	35
10666.7	19
10783.0	46
10813.0	22
10843.8	47
10951.3	16
11000.0	15
11057.9	14
11104.0	12
11463.8	44
11500.0	33
11704.0	20
11746.3	68
11790.1	66
12069.6	55
12146.4	54
12292.2	45

TABLE XIII - Microwave Absorption Frequencies and Relative Intensities Observed in Nitroglycerine Vapors (Run 29)

<u>Frequency, mc/sec</u>	<u>Intensity, arbitrary units</u>
10784.0	21
10845.0	32
11098.8	17
11466.4	22
11513.2	28
11704.7	17
11747.2	34
11793.1	36
12070.2	23
12139.5	45
12148.2	32
12295.0	35

TABLE XIV - Microwave Absorption Frequencies and Relative Intensities Observed in Smokeless Powder Vapors (Run 32)

<u>Frequency,</u> <u>mc/sec</u>	<u>Intensity,</u> <u>arbitrary units</u>
9751.0	12
9777.0	13
9826.1	15
10667.7	23
10783.9	31
10842.2	50
11462.0	15
11506.0	30
11700.9	20
11743.8	30
11789.0	34
12077.5	45
12155.0	35
12291.1	46

Except for a line at 10,844 mc/sec, all the lines in the Gelamite spectrum are separated from those of acetone. Any one or any combination of these lines could be used as a positive identification as well as detection method for explosive vapors.

The pressure of nitroglycerine in run 29 was about 12 μ Hg at the start, although the liquid was visible as a mist on the sampling tube. Air was added to raise the total pressure to 65 μ Hg to ensure thermal equilibrium of the molecules. Such a pressure of nitroglycerine would require about 16×10^{-8} moles, or 36 μ g. Recent measurements on $O^{18}Cl_2S^{34}$ at Hewlett-Packard Co. have shown that about 10^{-13} moles of the material can be detected in the presence of 100 μ Hg total pressure. If similar results could be obtained with nitroglycerine or EGDN, the microwave technique would rival the electron-capture device in sensitivity and, further, give a more positive identification of the molecules.

Other explosive compounds, namely, 2,4,6-trinitrotoluene and 2,4-dinitrotoluene, showed no absorption in the X-band. Since they have low vapor pressure, chemically similar ortho-nitrotoluene was examined (runs 23 and 27B). Pressures of 70 and 112 μ Hg were obtained, but no new lines above those of acetone were obtained.

TABLE XV - Microwave Absorption Frequencies and Relative Intensities Observed in Acetone Vapors (Run 27A)

<u>Frequency, mc/sec</u>	<u>Intensity, arbitrary units</u>
9203.4	21
9931.9	42
10159.1	30
10517.5	49
10535.5	33
10555.5	23
10569.6	20
10577.5	30
10580.5	44
10708.4	22
10728.7	25
10738.6	14
10748.8	77
10762.4	53
10826.4	14
10844.0	13
10853.7	21
10875.6	51
10916.4	38
10931.4	28
10941.0	15
10970.6	28
11018.5	38
11128.2	16
11134.3	25
11160.5	24
11173.3	44
11198.7	108
11226.4	28
11256.4	72
11283.1	44
11348.7	55
11360.2	35
11569.7	128
11584.3	70
11600.0	37
11631.2	30
11810.0	33
11825.8	15
11895.8	17
11960.0	25
12000.0	38
12087.5	26
12177.4	65
12229.4	45

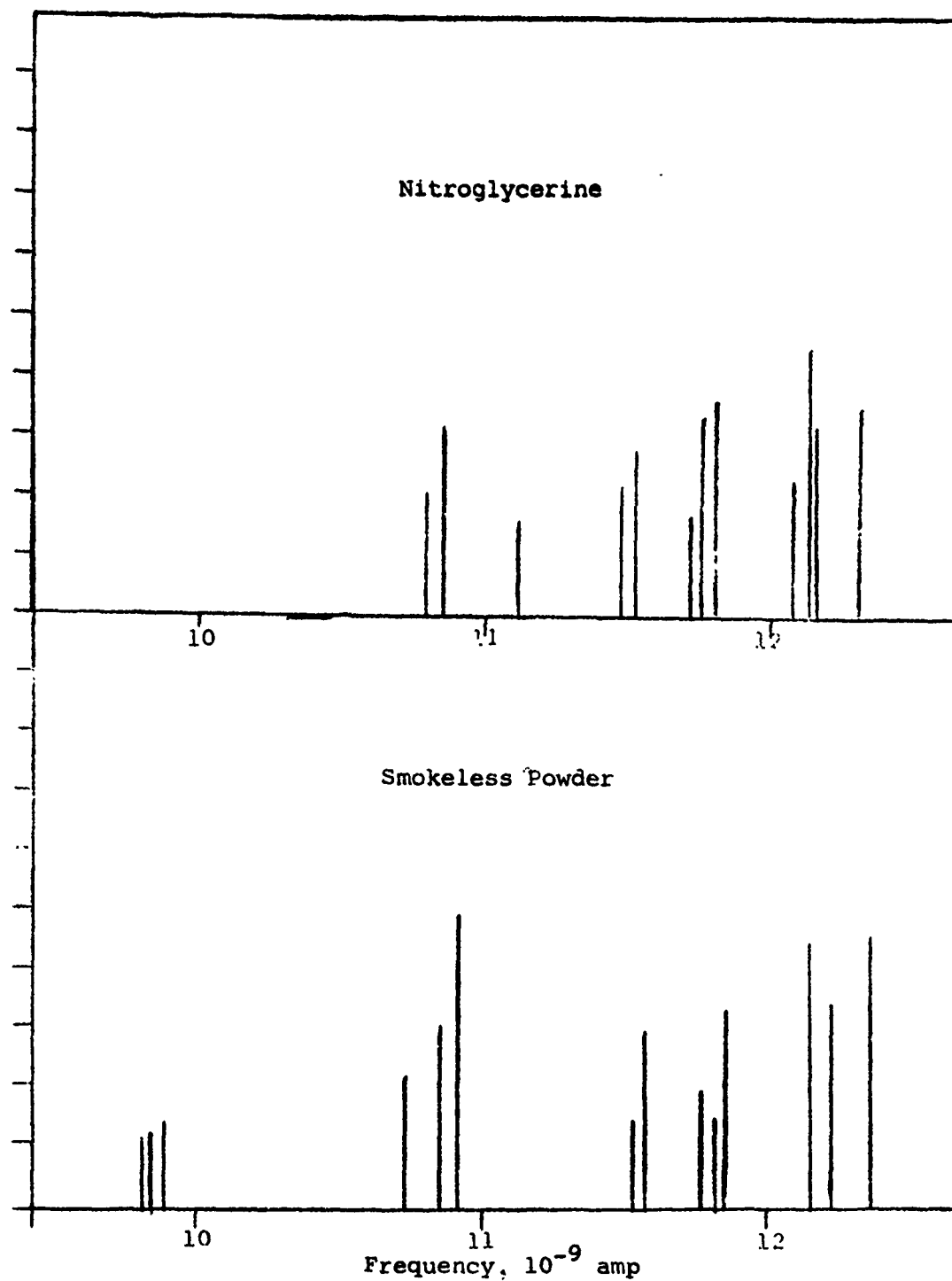


FIGURE 59 - Microwave Spectra of Nitroglycerine and Smokeless Powder

3.1.5 Conclusions and Recommendations

The experiments demonstrated the feasibility of detection of microgram quantities of bomb vapors by microwave absorption techniques. At present, the microwave spectrometer is a large, expensive, but versatile research instrument. However, engineers at the Hewlett-Packard Co. assure us that a much simpler machine operating at two or three fixed frequencies could be constructed in compact form at a reasonable cost. Because of time limitations, details of such a system were not discussed.

In a future program, additional samples of bomb vapors and pure samples of EGDN and nitroglycerine should be analyzed to determine especially the lowest concentrations detectable. After such studies, a microwave absorption detector sensitized specifically for EGDN and nitroglycerine might be considered. A cost estimate for the first prototype model could be prepared with assistance from the Hewlett-Packard Co. A theoretical study of the microwave spectra of EGDN and nitroglycerine could greatly assist in proving that the observed lines belong to EGDN molecules.

3.2 Emission Spectroscopy

McCormack, Fong, and Cooke (ref. 6) recently reported a gas-chromatography detector based on emission spectroscopy. They reported detection of hydrocarbons such as hexane in the range of 10^{-15} g, which is about 10,000 to 100,000 times more sensitive for detection of EGDN than the electron-capture system. Therefore, we investigated detection of explosive vapors by emission spectroscopy.

3.2.1 Principles

The emission spectrograph is a device for measuring and recording light emitted by any light source. In the case of chemicals, it is the light emitted by atoms and molecules, especially diatomic molecules. The chemical must be vaporized and excited by some means such as a high-temperature arc discharge, a plasma, or a burning flame. McCormack et al used as a light source plasma generated in argon gas at atmospheric pressure in a capillary tube. The power to maintain the plasma was provided by a microwave-generating machine.

When a few ions are introduced into the argon gas near the microwave cavity, the ions absorb much energy from the microwave field and the argon gas becomes very highly ionized. In this state, it is equivalent to a gas at thousands of degrees centigrade and is referred to as a plasma. If other materials or vapors are present in the argon, they are also ionized and are excited by collision with the argon ions or directly by the microwaves. When the excited ions and molecules release their excess energy by recombination, they emit light in a broad spectrum from the infrared through the visible and on to the ultraviolet.

This light is conducted to the entrance slit of the spectrograph, as shown schematically in Figure 60. The light then goes through a prism or is reflected from a grating, where it is spread out into a spectrum. By rotating the grating, various wavelengths of light pass across the exit slit and on to a light-sensitive tube, called a "photomultiplier tube." This converts the light intensity into a proportional electrical signal, which can be amplified and recorded on a standard strip-chart recording potentiometer similar to the ones used in gas chromatography.

Alternatively, the exit slit and the photomultiplier tube can be removed and a photographic plate used. This gives a permanent record of the entire spectrum, but is not suitable for gas chromatographic detection.

For use as a chromatographic detector, the prism or grating is set to monitor a certain wavelength at the exit slit and the photomultiplier. This wavelength is chosen to correspond to the light that is characteristic of certain transitions in the materials to be detected. If that material then enters the plasma, light of the required wavelength is emitted and a peak is displayed on the recorder.

Thus the instrument can be operated in one of two modes. In the first mode, vapors are fed through the tube at a constant concentration and the grating rotated to allow recording of the spectrum from about 8000 to 2500 Å. If emission lines that are not in the spectrum of pure argon appear, they can be attributed to the sample vapors.

After such lines are found, the machine is operated in the second mode. The grating is set to a certain wavelength, and pure argon is passed through a gas-chromatograph type of column to establish a base line. A sample of the vapors is then injected into the system, much as in ordinary chromatography.

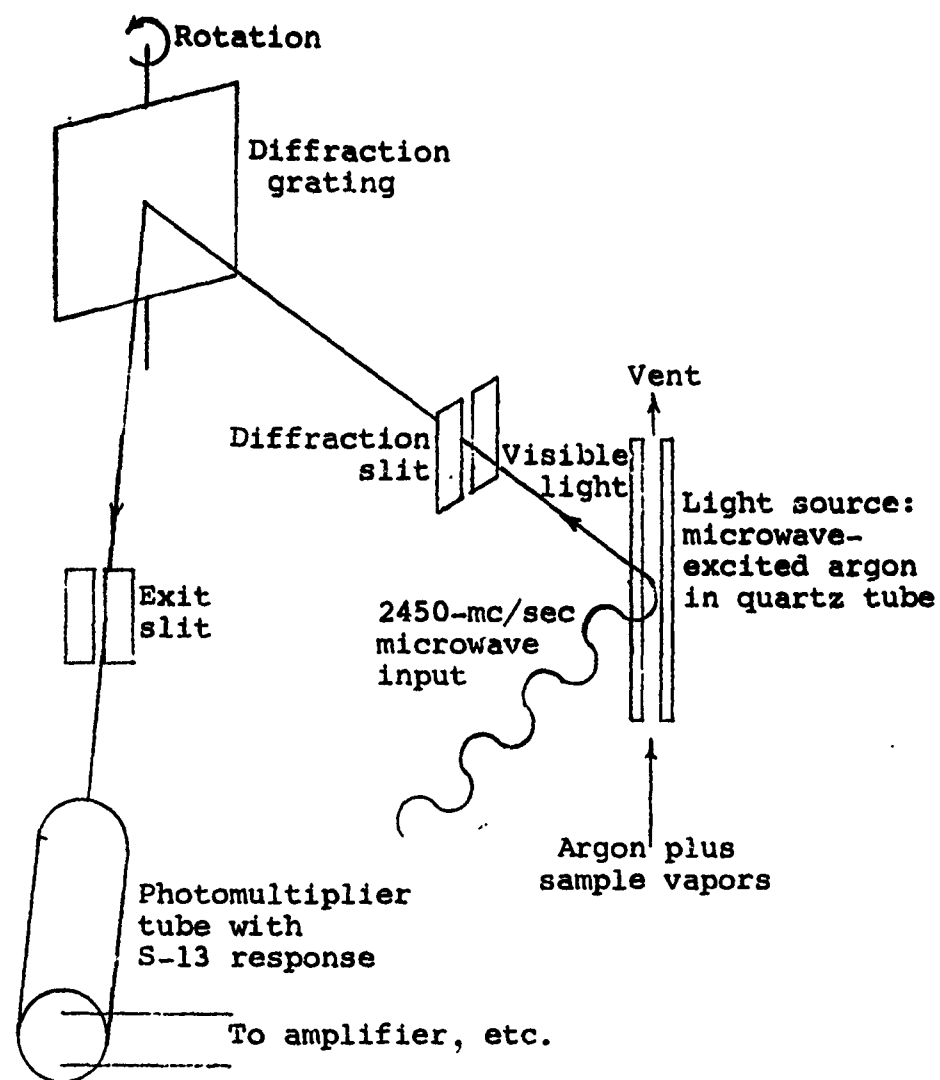


FIGURE 60 - Apparatus for Microwave-Heated Argon-Plasma Emission Spectrometry

As the vapors pass through the column and into the plasma, they become excited and emit their characteristic light and pass out of the plasma. In this way, the photomultiplier, etc. produce a peak on the recorder as the vapors pass through the plasma.

3.2.2 Experimental Procedures

The experimental setup used to examine the spectra of various explosive vapors is shown schematically in Figure 61. Argon gas of 99.996% purity from the gas tank was passed through a cold trap to remove any high-boiling hydrocarbons and other low-vapor-pressure materials. Dry ice was used as the refrigerant, because liquid nitrogen freezes argon to a solid. The stripped argon passed through a tubular oven containing a tube filled with titanium sponge metal. The oven was operated at 950°C for 24 hr with argon flow to remove any titanium tetrachloride remaining from the preparation of the titanium sponge. Then the temperature was reduced to 850°C for operation.

The argon passed through a sampling tube and on to the quartz tube in the microwave cavity. There the argon and sample vapors were excited by the ionized gas and emitted their characteristic light. Some of this light, which was emitted in all directions, passed through a quartz tube perpendicular to the capillary. This, in effect, brought the capillary light source up to the entrance slit of the spectrometer.

This arrangement was found to be necessary because the residual impurities in so-called "pure" argon are sufficient to cause light emissions in the regions where argon does not emit and where explosive vapors might emit. The hot titanium removes residual gases such as water, carbon dioxide, oxygen, nitrogen, methane, and ethane. Helium, neon, and hydrogen would not be removed.

The spectrometer used was a model SP-900 flame spectrophotometer from Unicam Instruments, Ltd., Cambridge, England. It is a folded-path prism spectrometer with a dispersion of about 25 Å/mm.

The microwave unit, from Raytheon, Waltham, Mass., was a diathermy machine used most frequently in clinical medicine. This instrument was a model CMDS with a maximum power output of 125 w at a frequency of 2450 mc/sec.

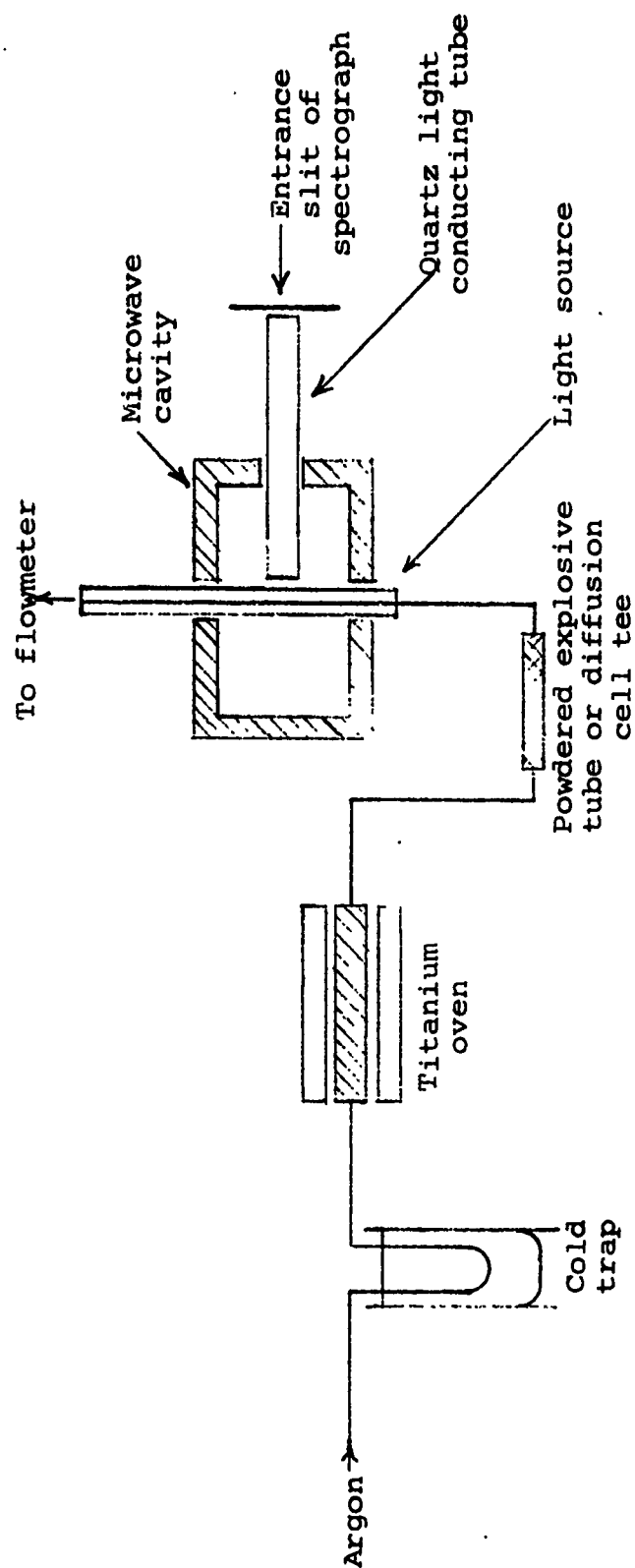


FIGURE 61 - System for Studying Explosive Detection by Emission Spectroscopy

The microwave cavity was made by Aircom of Boston, Mass. It consisted of a hollow rectangular tube 2-1/4 in. high by 4-1/2 in. wide by 34 in. long in three sections. The first section converted the a-c electrical power at 2450 mc/sec to an electromagnetic or a light wave at the same frequency. The quartz tubes carrying the argon and the light passed through the second section. Two holes in the center of the 4-1/2-in. walls allowed the quartz capillary to pass through. Another hole in the 2-1/4-in. wall admitted the quartz rod for guiding the light to the spectrometer. The third section was an adjustable tuner to allow coupling of the microwave power to the quartz tube in the second section. It reflected the microwave power to give a maximum at the desired position in the second section, i.e., at the capillary tube.

In the region that was important for the spectral studies -- below 4000 and down to 2500 Å -- the pure argon spectrum was free of emission lines except for a few intervals. Lines appearing in argon-free regions can be used to detect the presence of material in the carrier gas.

3.2.3 Test on Carbon Disulfide

Gun powder might contain some volatile carbon sulfur compounds, since it is composed of elemental carbon and sulfur. McCormack et al. (ref. 6) mentioned the detection of carbon disulfide at a level of 10^{-9} g/sec and a flow rate of 50 ml/min.

To investigate the possibility of detection of small amounts of sulfur compound, the following setup was devised. Figure 62 shows an apparatus for producing a known concentration of a volatile material in air. The liquid was placed in a bulb sealed on the end of a 1-mm-ID capillary tube 1 to 10 cm long or longer. This was attached to a tee joint in the tube from the argon tank and the furnace. After a few hours, in most cases, a concentration gradient established itself along the capillary from the bulb to the tee.

The concentration of vapor in the gas flowing across the tee is given by the relation:

$$C = D \frac{A(N_s - N_o)}{dF} \quad (8)$$

where

- C is concentration of carbon disulfide in argon carrier gas
- D is diffusion coefficient of carbon disulfide in argon
- A is cross-sectional area of capillary
- d is length of capillary
- F is flow rate of argon carrier gas
- N_s is concentration of carbon disulfide vapor in bulb
- N_o is concentration of carbon disulfide at outlet of capillary

A capillary of 1-mm ID was used. Therefore the cross-sectional area was $7.85 \times 10^{-3} \text{ cm}^2$. In the first run, a capillary 1 cm long was used, but so much carbon disulfide came out that the argon plasma became unstable and did not stay lit. A 3.0-cm length was found to be best.

The diffusion coefficient of carbon disulfide vapor in air is reported in the Handbook of Physics and Chemistry, 1962, page 2275, as $0.102 \text{ cm}^2/\text{sec}$. We assumed that this would be a good approximation to its diffusion coefficient in argon. The vapor pressure of carbon disulfide was also given in the Handbook and found to correspond to a concentration of 1.47 mg/cc at 24°C , the temperature of the bulb.

Assuming the concentration of the vapor at the outlet to be negligible compared to that of the bulb, it was calculated that $393 \times 10^{-9} \text{ g/sec}$ would escape from the capillary into the tee. Since a flow rate of 45 cc/min was used, the concentration of carbon disulfide in the argon carrier gas would be about $5.2 \times 10^{-7} \text{ g/cc}$. Thus, the 3-cm x 1-mm capillary gave a dilution factor of about 3500.

This concentration, then, was fed to the plasma source, and the resulting spectrum was analyzed from about 8000 to 2500 Å. Except for the appearance of large peaks at 3883 and 3536 Å, due to CN bands, and some changes in the relative intensities of the argon lines, the spectrum was little different from that of plain argon. However, weak lines appeared near 2600 Å. Under optimum conditions of slit width, amplifier gain, and noise suppression, the spectrum in Figure 63 was obtained. This can be compared to that reported by McCormack, shown in Figure 64.

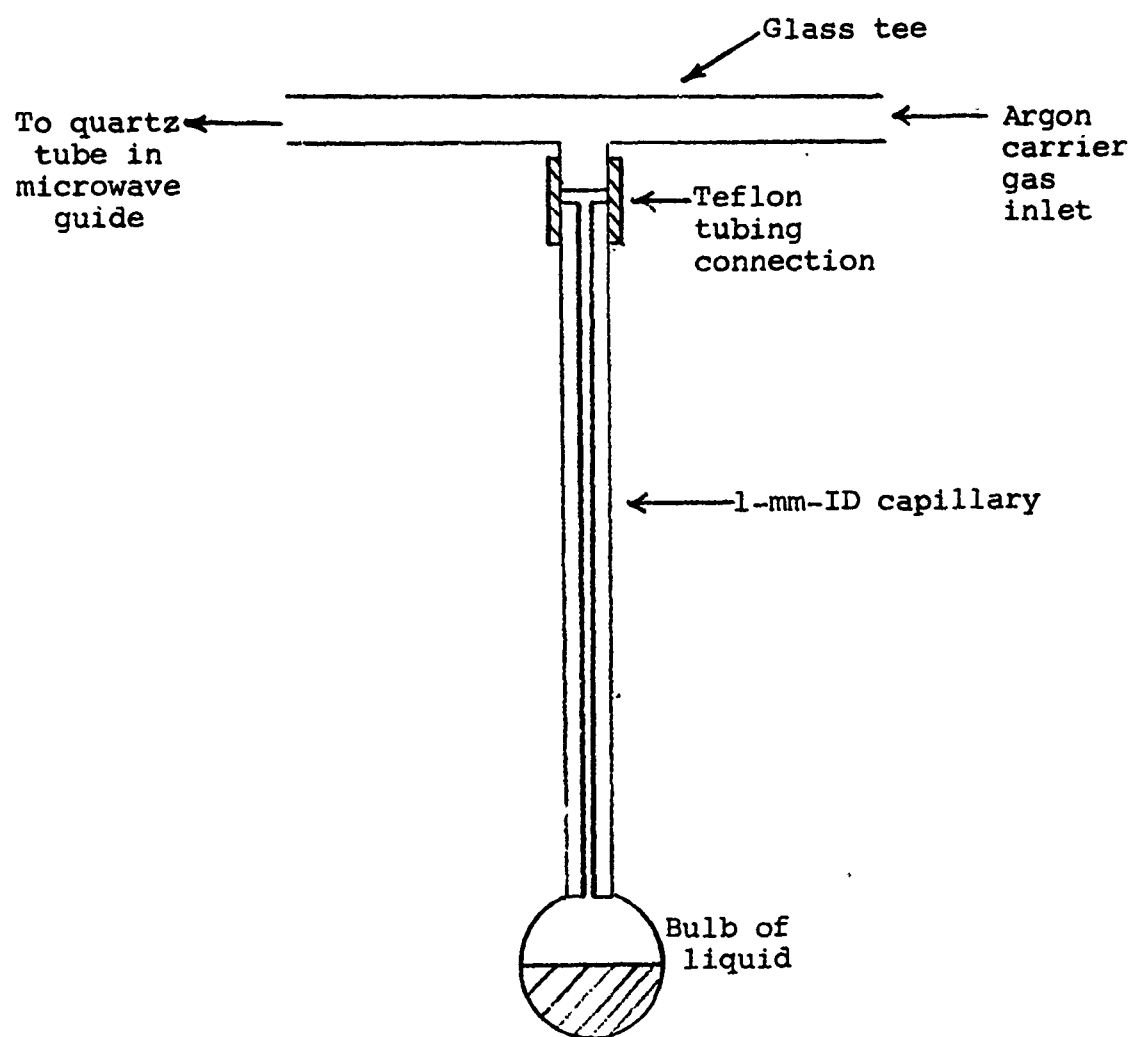


FIGURE 62- Diffusion Dilution Apparatus

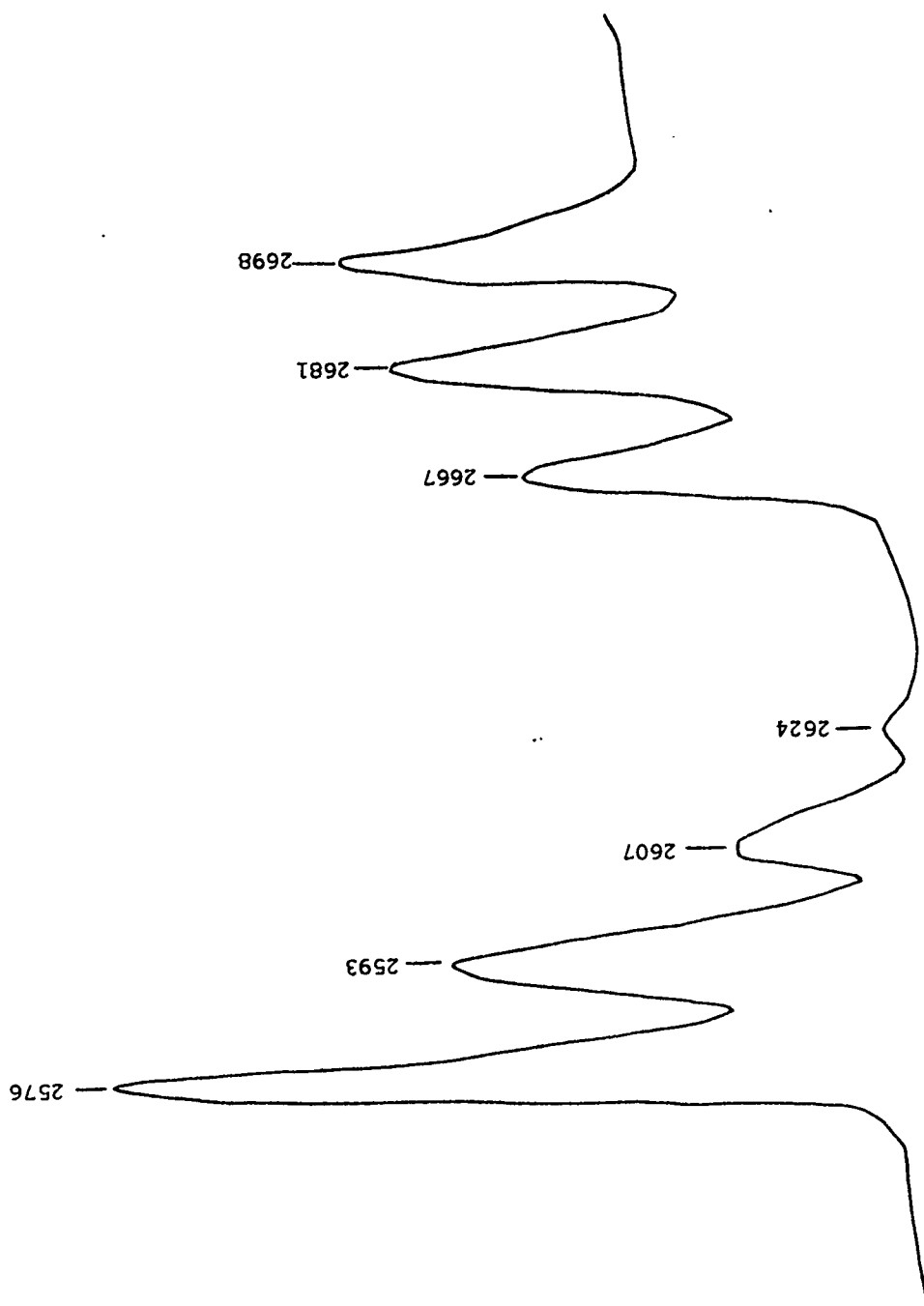


FIGURE 63 - Spectrum of Carbon Disulfide Vapors in the Ultraviolet Region

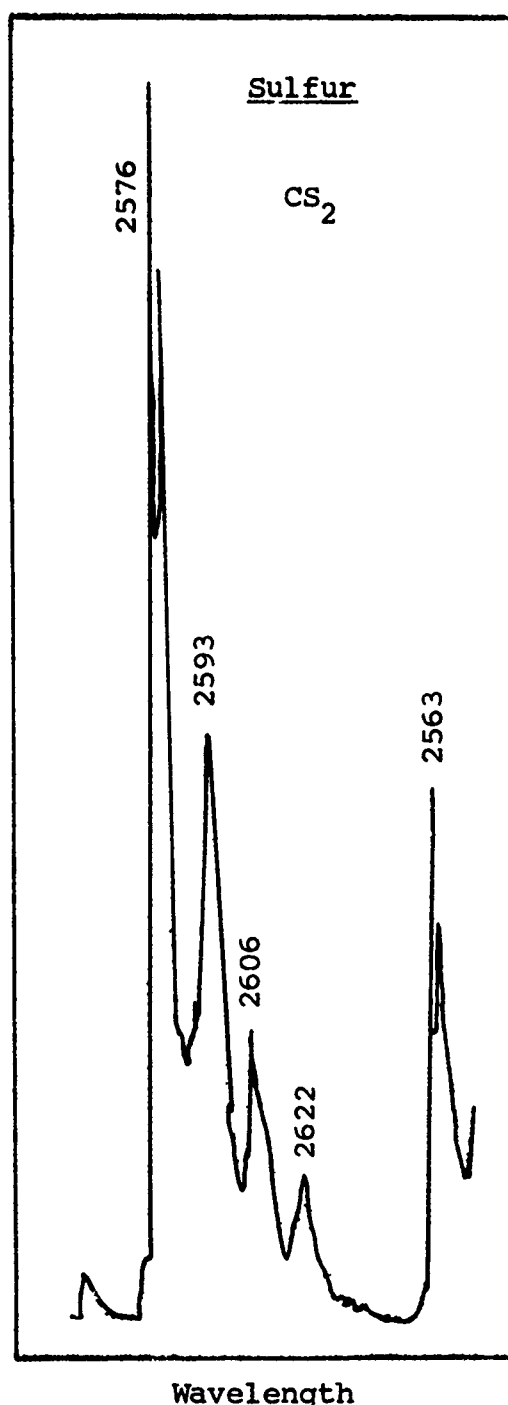


FIGURE 64 - Spectrum of Carbon Disulfide as Reported by McCormack et al (Taken from ref. 6)

The concentration to get the spectrum in Figure 63 was about 5×10^{-7} g/cc, and the rate was about 4×10^{-7} g/sec. It is estimated that a concentration about 10 times lower could be detected by increasing the amplifier gain, etc. McCormack, however, claims that a rate of 1×10^{-9} g/sec is measurable; this is about 40 times smaller than our estimate. Since time was limited, experiments to explain this discrepancy were not undertaken.

3.2.4 Experiments on Explosives

After completion of the above experiments demonstrating that the system was working, a series of runs on explosive powders was undertaken. After purified argon was passed over a few grams of the powdered sample for several hours or overnight, the emission spectrum was run from 8000 to 2500 Å at a gain of 2, an electric band (noise control) of 3, a slit width of 0.01 mm, and a microwave power input of about 50% (67 w).

The resulting spectrum of the vapors and argon was directly compared with the argon spectrum alone. In each run, large amounts of light were emitted at 3883 and 3586 Å, where cyanogen (CN) bands occur, and at 3082 Å, where hydroxyl (OH) bands occur. These regions are empty on the pure argon spectrum.

Then the region below 3000 Å, which is especially free of argon lines and other radiation, was examined at a higher gain, 6, and a slit width of 0.1 mm. This increased the sensitivity by a factor of 10 to 100; thus any emissions were measured under conditions of less noise and lower sensitivity.

3.2.5 Results and Discussion

The conditions and the results of the experiments on explosive vapors are listed in Table XVI. Only for Gelamite-II and 2,4-dinitrotoluene were fairly strong characteristic spectra different from all the others obtained. The spectrum of Gelamite-II is shown in Figure 65. Whether this spectrum is due to EGDN or some other component is not known. The peak at 2824 Å appeared weakly in the other materials except carbon disulfide. The spectrum from 2,4-dinitrotoluene is shown in Figure 66. Notice that the lines labeled 2961 and 2947 also appear in the Gelamite-II spectrum, but slightly displaced and smaller. Since 2,4-dinitrotoluene is a minor component of Gelamite-II, these data may represent the first detection of explosive vapors by emission spectroscopy.

TABLE XVI - Summary of Emission Spectrometer Experiments

Vapor Source	Number of Runs	Flow Rate, cc/min	Microwave Power	Gain	Slit Width, mm	Electric Band	Response
Carbon disulfide	3	45	70	4	0.1	3	See Figure 63.
Gun powder	5	36	20	4	0.1	3	Very little at 2822 Å. None at 2576 Å.
Gelamite-II	3	49	100	4	0.1	2	Some at 2900 Å; see Figure 65.
2,4-dinitrotoluene	2	25	50	5	0.1	3	Little at 2961 Å and 2947 Å; see Figure 66.
Composition B	2	25	50	5	0.1	3	Very slight at 2822 Å.

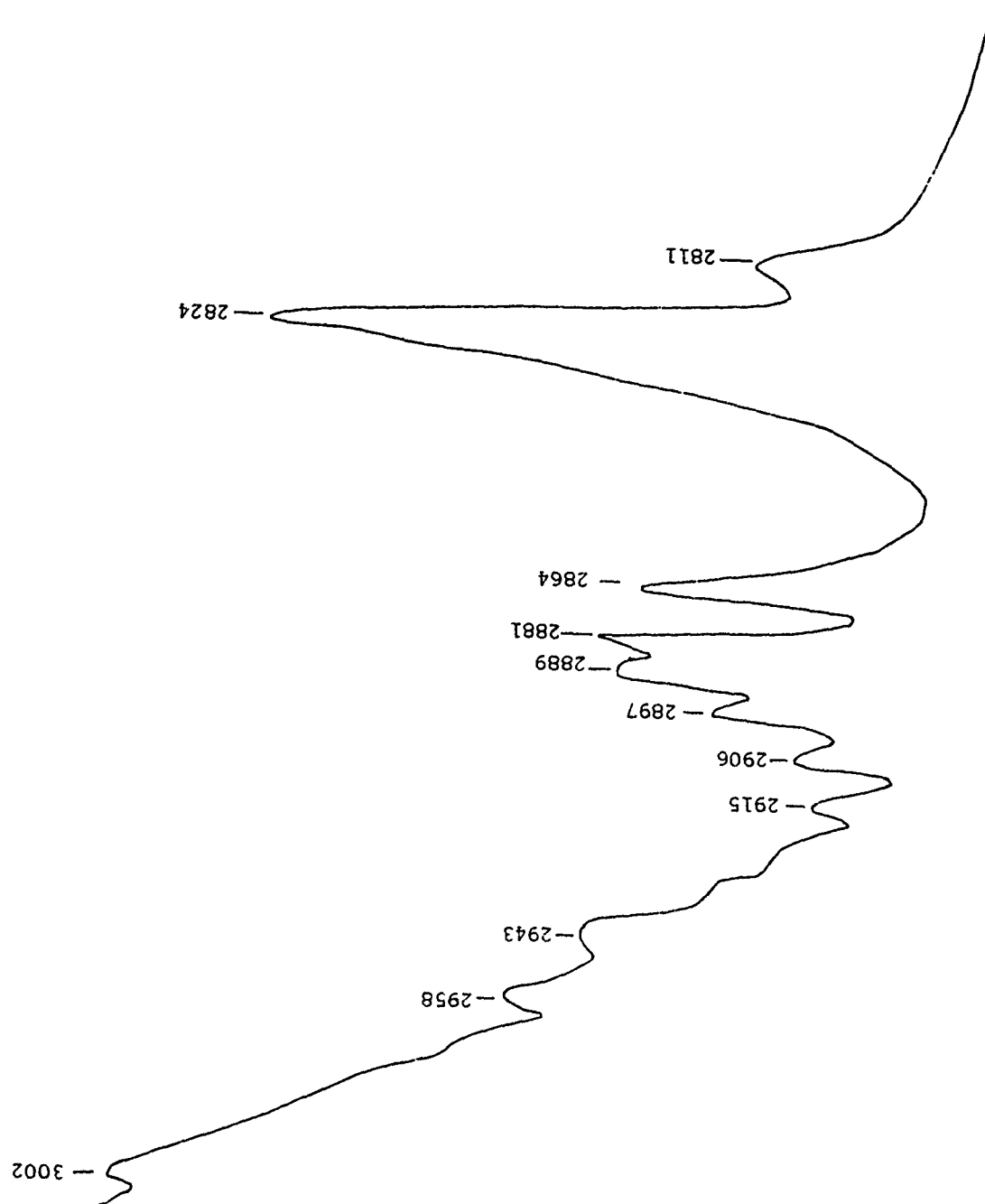


FIGURE 65 - Spectrum of Gelamite-II vapors

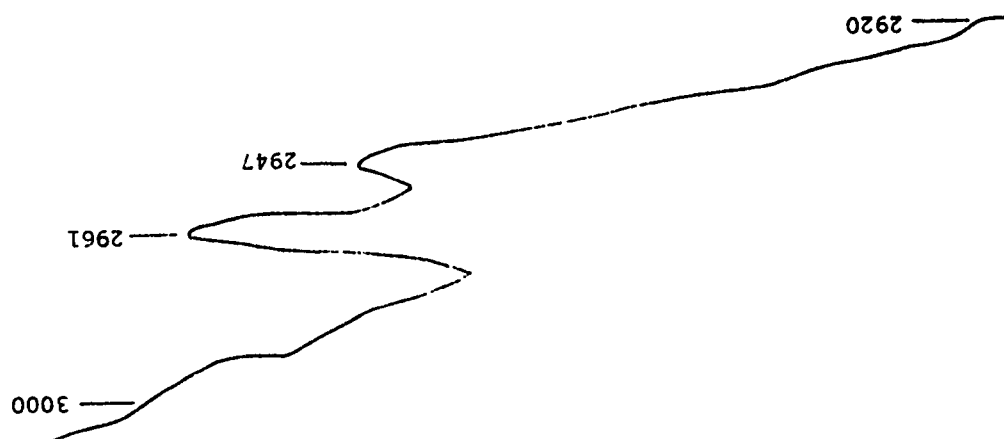


FIGURE 66 -- Spectrum of 2,4-Dinitrotoluene Vapors

Many more experiments under various conditions will be necessary to determine the origin and the sensitivity of these emission lines. A rough estimate of the amount of 2,4-dinitrotoluene entering the detector from the pure material and Gelamite can be obtained from the data taken during the first year's work. The vapor pressure of 2,4-dinitrotoluene is roughly 10^{-3} mm Hg, which corresponds to about 10^{-9} g/cc. 2,4-Dinitrotoluene in 2,4,6-trinitrotoluene has a vapor pressure less by factor of 10 or 20, roughly 10^{-10} g/cc. The apparent peak sizes in Figures 65 and 66 are in about the same ratio, 10 or 20 to 1.

It appears that 2,4-dinitrotoluene from Gelamite-II is being detected in the range of 10^{-10} to 10^{-11} g/sec. This can be compared with McCormack's data in his Table II. He reports detection of various materials by emission in the range of 10^{-7} to 10^{-16} g/sec, with most around 10^{-10} g/sec. This appears to be about the sensitivity we achieved.

All the materials studied exhibited intense emissions from cyanogen and hydroxyl radicals. Because of time limitations, it was not possible to investigate the use of the spectrometer as a gas chromatographic detector. It may be possible to use a separation column to isolate components of explosives while monitoring the cyanogen bands, where the detection sensitivity is extremely high.

In the case of black powder, we were unable to detect emission lines that would be characteristic of sulfur. Hence, if sulfur compounds were evolved by the black powder, their concentration was below the detection limit of the microwave device. Preconcentration of vapors was not attempted.

The emission spectrum of black powder, at the vapor concentration tested, did not exhibit any other characteristic features that could be used for detection of its presence.

3.3 Flame Ionization Detector

Since neither electron capture nor microwave-heated plasma emission were found to be useful for detection of black powder vapors, these vapors were investigated by a flame ionization detector. The flame ionization detector detects vapors of all organic substances, and discrimination of substances can be achieved by a gas chromatographic partition column placed upstream of the detector. The combination of the partition column and the flame ionization detector is routine in gas chromatography.

An Aerograph 200 instrument was used. High-purity helium was passed through a glass tube packed with black powder. The vapors picked up from the powder by helium were cryogenically collected in a stainless-steel capillary and were introduced into the gas chromatograph for analysis by routine means.

Many peaks, each representing a different vapor component, were observed. As the vapor collection was continued, the peak pattern changed, many peaks decreasing in size. It was concluded that at the routine sensitivity levels none of the peaks were truly characteristic of gun powder, but probably represent artifacts produced by various environmental organic vapors adsorbed by the powder, most probably by the carbon component. Thus, a characteristic pattern from black powder has not been obtained so far.

Possibly, slow reactions at the surfaces of the powder particles between its components (sulfur and carbon) and the oxygen and/or the moisture in air produce characteristic vapors. This possibility was not studied, as we did not want to divert effort from the principal task of developing a bomb detector for high explosives.

4.0 ENGINEERING MODEL

The objective of the design and construction of the engineering model of the bomb detector was to combine and automate the steps involved and to demonstrate the operation of the assembled model in detection of concealed dynamite.

One of the primary tasks in formulating the design was to select the area size for the gold adsorbent surface. If air contains 0.1 ppb EGDM, which was an estimate for the concentration expected in airplanes, the required area can be approximated as follows. Before they adsorb, EGDM molecules must diffuse through a boundary layer of air at the gold surface. Since 0.1 ppb corresponds to 2.5×10^9 molecules/cc of air, the maximum number of molecules that can be delivered per second to 1 cm² of surface is:

$$n = D \frac{2.5 \times 10^9}{d}$$

The value of D, the diffusion coefficient of the molecules in air, is of order of 0.1 cm²/sec⁻¹. The value of d, the thickness of the boundary (nonturbulent) air film, depends on the aerodynamics of airflow past the surface. Assume that d = 0.1, which is valid for moderate turbulence. Then $n = 2.5 \times 10^9$ molecules/sec cm.

Previous experience indicated that the electron-capture detector can detect 10⁻⁹ g of EGDM, which corresponds to 4×10^{12} molecules. To deliver this amount to the adsorber in 10 sec, provided that all subsequent sample transfer and analysis steps are loss-free, the adsorber area must be:

$$\frac{4 \times 10^{12}}{10 \times 2.5 \times 10^9} = 160 \text{ cm}^2$$

However, several considerations must be taken into account. On the one hand, the sample collection, transfer, and analysis steps cannot be expected to be fully efficient. On the other hand, a lower d can be reached by higher airflow rates past the gold surface. The two factors work in opposite directions. To compensate for additional losses and still stay within practical size limits, an area of 1000 cm² was selected for the gold adsorber surface in the engineering model.

With 2.5×10^9 molecules/cc in air, and at least 4×10^{12} to be available at the detector end of the device, EGDN molecules from 1.6 liters (approximately 0.05 ft^3) would have to be totally extracted and delivered loss-free to the detector through all intermediate steps. Since neither total extraction nor loss-free manipulation is possible in an engineering model, the amount of air to be fed past the gold surface should be much larger.

An arbitrary figure of at least 100 ft^3 was taken, which is 2000 times higher than the theoretical minimum. This figure satisfied reasonable geometry of passages for airflow past gold surfaces, provided that the surfaces are not too far apart and that the air pressure drop in passages is low. Actually, a somewhat higher flow rate was achieved in the engineering model. Since it was desired to hold the air sampling time to 1 min or less, 100 cfm or more must be passed through the adsorber.

The disparity between the dimensions of the gold surfaces adsorber, which must pass 100 cfm or more air and have a gold surface of 1000 cm^2 , and the analysis section, in which the carrier gas flow is below 100 cc/min, necessitated introduction of an intermediate step: transfer of EGDN molecules from a 1000-cm^2 gold surface to a much smaller, secondary adsorber, which could be in series with the analytical partition column upstream. The choice for the secondary adsorber was a gold tube 3-in. by $1/8$ in. OD. Flash desorption from this tube into the analytical carrier gas flow is possible at normal carrier gas rates.

Consequently, studies were conducted by adsorbing EGDN on larger gold surfaces from dilutions of its vapor in air, transfer of the adsorbed EGDN to smaller gold surfaces, and subsequent desorption and analysis in the manner described in Section 2.5. To establish the nature and the magnitude of electron-capture detector response that can result from operation of valves directing the carrier gas flows, Teflon solenoid valves intended for use in the engineering model were also tested in the bench-scale apparatus. The flow direction changes were arranged in the same way as in the proposed model.

4.1 Transfer of EGDN from Large to Small Gold Surface

The studies on adsorption of EGDN on a larger gold surface (primary adsorber) and transfer to a smaller gold surface (secondary adsorber) dealt with several surface area ratios

and with the effect of temperature of the secondary adsorber on its collection efficiency. The EGDN vapor mixtures at high dilutions were prepared in a continuous-flow apparatus or were taken from a large room into which controlled amounts of EGDN vapor were introduced. In all cases, a 3-in.-gold tube, 1/16 in. ID, was used as the secondary adsorber. It had an adsorptive area of 3.7 cm².

4.1.1 Primary Adsorber with 13.8-cm² Area

The initial study of EGDN utilized a 12-in. gold tube, 1/8-in. OD by 1/16-in. ID, with an adsorptive area of 13.8 cm² as the primary adsorber. This is relatively small. The EGDN source consisted of the bench dilution apparatus (Figure 46) using dry bottled air.

The sample partition and detection system used is illustrated in Figure 67. This system is essentially the same as that described in Section 2.5, except for the addition of the primary adsorber gold tube and a box for the 3-in. gold tube. The box served to ensure even and total heating of the 3-in. gold tube. It was constructed of Transite, a commercial insulating material composed of compressed asbestos held in a matrix of high-temperature binder. The box completely covered the 3-in. gold tube except for a circular hole in one wall, where the heat gun was placed during heating. It was also made mobile, so that it could be removed after heating, to allow the tube to cool.

The various tests for cleanliness (mentioned in Section 2.5.2) were performed on the two gold tubes and the dilution apparatus. The flows of air were then set for the desired dilution ratio, and the clean 12-in. primary adsorber gold tube was removed from the gas chromatograph and put into the dilutor sample port. When the primary adsorber was removed from the analytical section, it was immediately replaced with a dummy tube of Teflon, to prevent contamination of the analytical section. The primary adsorber was exposed to EGDN vapors for 5 min and then placed back into the analytical system.

After the analytical system carrier gas flow returned to normal, the 12-in. gold tube was heated to 80°C with a heat gun. This heating released the adsorbed EGDN, which was carried by argon into the clean 3-in. secondary adsorber gold tube and reabsorbed there.

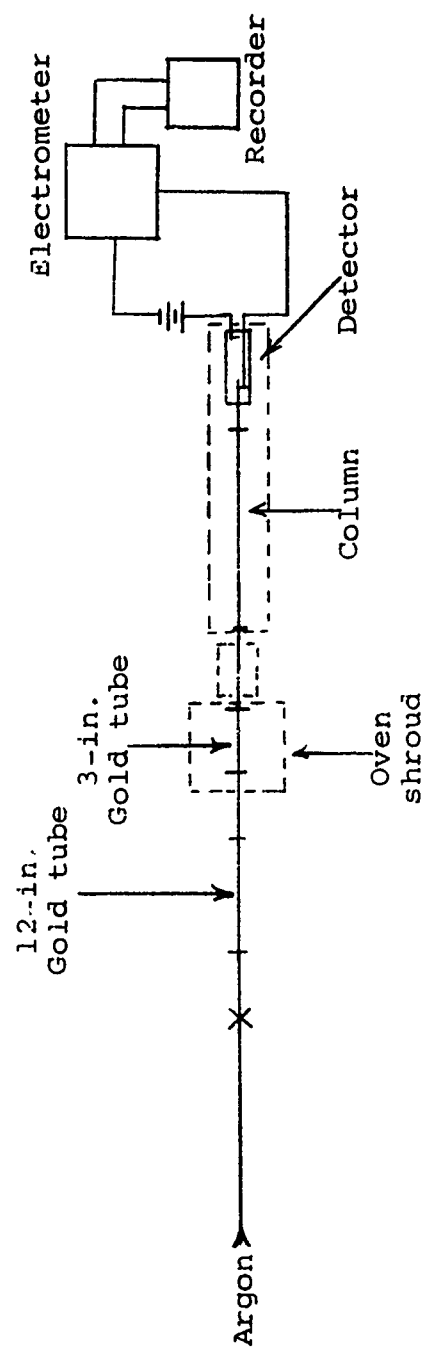


FIGURE 67 - Bench Apparatus Used in Initial EGDN Vapor-Transfer Experiments

After the primary adsorber had cooled, the Transite box was placed around the secondary adsorber, which was then heated to 80°C. This heating released the readsorbed EGDN from the gold surface and introduced the vapor into the partition column with the argon carrier gas stream.

In the initial experiments, the secondary adsorber was at room temperature when receiving EGDN vapor from the primary adsorber. Although the 3-in. gold tube retained sufficient EGDN to enable detection, approximately 90% of the vapors was not retained, leaked through the 3-in. gold tube, and was detected prematurely. Further experimentation with the 3-in. gold tube at various temperatures below ambient revealed that 95 to 98% of the EGDN was retained with the secondary adsorber tube at 0°C. Using the above procedure and temperature, we were able to consistently sample, transfer, and detect EGDN at a dilution of 1:100,000.

4.1.2 Primary Adsorber with 340-cm² Area

The second phase of the transfer experiments involved the replacement of the 12-in. gold tube (surface area 13.8 cm²) with gold adsorptive medium with a surface area of 340 cm². (In the engineering model, the proposed primary adsorptive gold surface had an area of 1040 cm²). The increase in surface area to 340 cm² approached the proposed area and enabled us to investigate the transfer phenomenon on a scale more closely resembling the final instrument.

The 340 cm² of gold was placed inside a modified Liebig condenser. The condenser tube had a 3/8-in. ID and was 15 in. long. The jacket had a capacity of 500 ml. To desorb the EGDN, it was filled with preheated water.

The temperature of the gold surface was monitored by a thermocouple placed in a well. Nichrome wire was wrapped around the outer surface of the jacket so that the gold surface could be cleaned by much stronger heating (above 100°C) after sampling and transfer. Figure 68 shows a cross-sectional diagram of the condenser and the configuration of the gold surface. The gold surface was in the form of foil 5 mils thick.

The apparatus used to transfer the EGDN vapors from the large primary adsorber to the 3-in. secondary adsorber is shown in Figure 69.

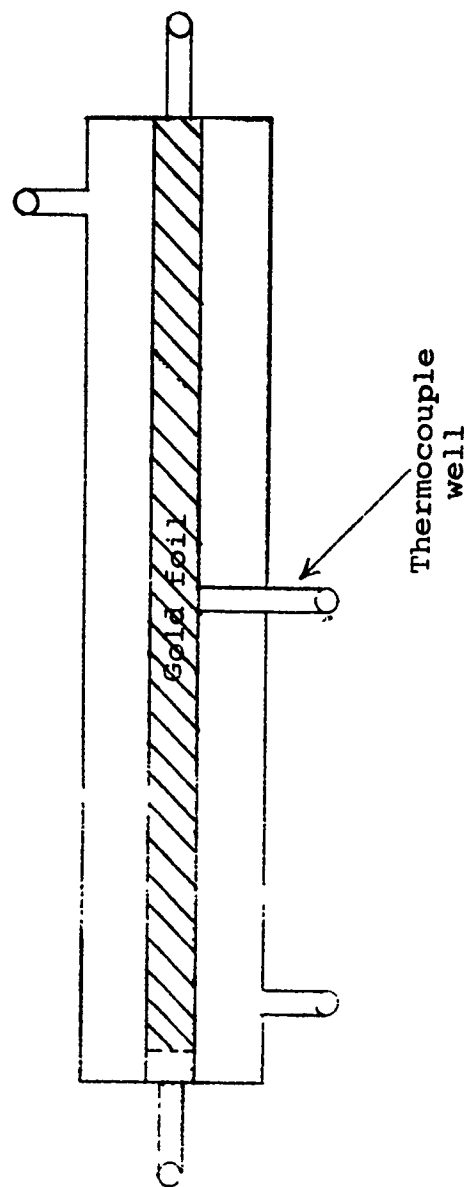


FIGURE 68 - 340-Cm² Primary Adsorber

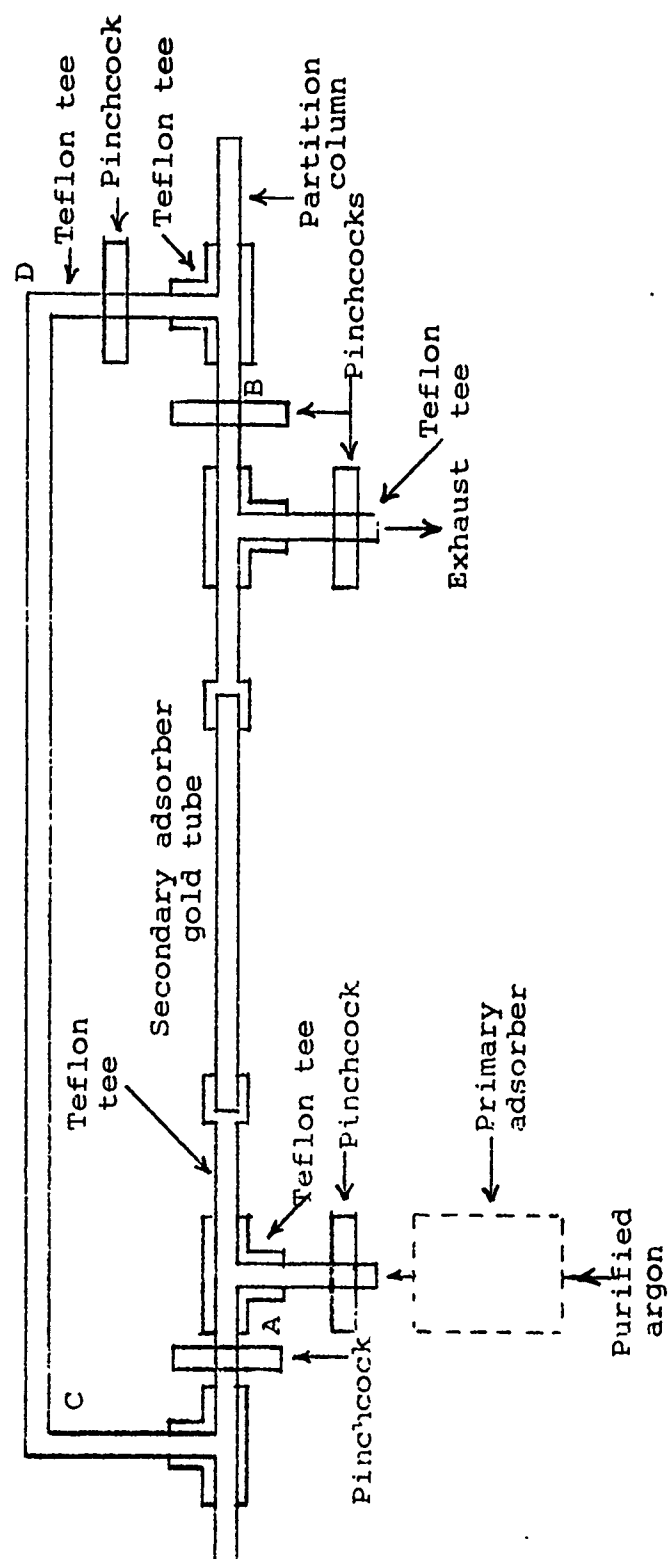


FIGURE 69 - Bench Apparatus with Fixed Secondary Adsorber

At the point labeled A, 15 ft of copper tubing was coiled into a capillary, so that the pressure drop resulting from the insertion of the large primary adsorber and the secondary adsorber during transfer would have no more than a negligible effect on the gas flow. The gas used for transferring was high-purity argon.

The EGDN source used was the bench dilution apparatus described in Section 2.5.1. The dilutor was cleaned and checked in the same manner as mentioned previously. Before the first sampling, the primary adsorber was flushed with acetone and heated to 200°C to clean out any impurities present on the surface of the gold foil. The dilutor was then set for the EGDN concentration desired, and the primary adsorber was placed into the sample port. The sample was collected at room temperature for 5 min.

The adsorber was then removed from the dilutor and connected to the transfer apparatus with the transfer gas flow still off. The hot-water lines were connected to the water jacket; and the clean secondary adsorber, packed in crushed ice, was connected with Teflon tubing to the primary detector.

The primary adsorber tube was heated to 80°C and was maintained at this temperature by a slow flow of heated water through the jacket. The argon flow was started and the transfer begun. The argon gas flow was kept at 150 cc/min for 2 min and then shut off. The cold secondary adsorber, still covered with crushed ice, was put back into the analytical section. The ice was removed, and the secondary adsorber was heated to 80°C for the analysis and detection step.

EGDN was successfully detected by using this apparatus and procedure. However, the peaks were sometimes too wide, irrelevant broad peaks occurred, and bleeding of substances produced a response in the electron-capture detector. The difficulties were traced to contaminants from air and perhaps oxygen in the air. The contaminants, together with traces of moisture, condensed in the secondary adsorber while it was being carried from the EGDN transfer apparatus to the analytical section of the bench apparatus.

Other problems were impurities in the argon carrier gas used in the analytical section. Since the secondary adsorber was at 0°C while in the analytical section, it collected the impurities from argon and, upon heating to 80°C, released these together with EGDN.

Another problem was the Teflon links in the analytical system. These were at room temperature or higher but still somewhat below the column temperatures. They retained EGDN and bled it off during subsequent tests.

4.1.3 Fixed Secondary Adsorber

The above problems were solved by modifying the system as shown in Figure 69. The principal features of the operation of this system were as follows.

The secondary adsorber was permanently installed in the analytical section. The vapors collected in the primary adsorber were transferred into the secondary adsorber by argon, which, before it entered the transfer system, was purified by passage through a molecular sieve column kept at -80°C . During the vapor transfer, the primary adsorber was heated by hot water, while the secondary adsorber was kept at 0°C by crushed ice. During the vapor transfer, the partition column section was fed a separate stream of purified argon gas. All Teflon connections and valves (actually pinchcocks on Teflon tubes at this stage) were kept hot (about 100°C) by electrical resistance heaters, to prevent retention of EGDN vapor.

For the analytical sequence, the primary adsorber was disconnected; and argon was arranged to flow through the secondary adsorber, partition tube, and electron-capture detector in series. After stabilization of the flow, analysis was started by removing ice from around the secondary adsorber and heating the adsorber to 80°C with a hot airstream from a heat gun.

This fixed adsorber system with heated connections eliminated many disturbing effects that were observed in the previous system, and more accurate EGDN detection became possible. Figure 70 shows two typical EGDN peaks recorded with the improved apparatus.

4.2 Sampling from Room Air

With the successful development of the EGDN transfer process from a larger (340 cm^2) to a smaller (3.7 cm^2) gold surface, experiments with EGDN vapor sampling from open room air became feasible. These experiments were conducted in a 100,000-liter (3500 ft^3) room arranged as shown in Figure 71.

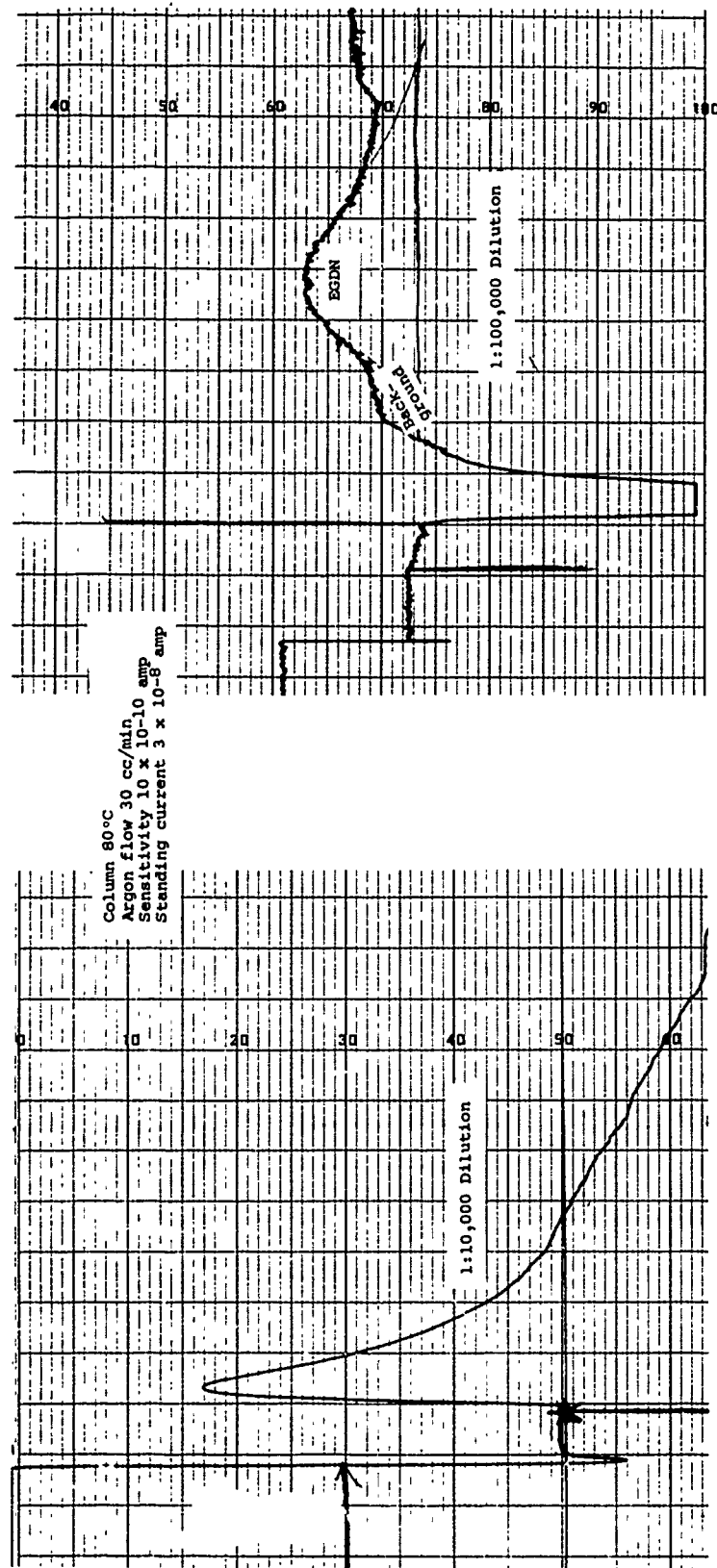


FIGURE 70 - Typical Peaks Obtained at 1:100,000 and 1:10,000 Dilutions with Fixed Secondary Adsorber

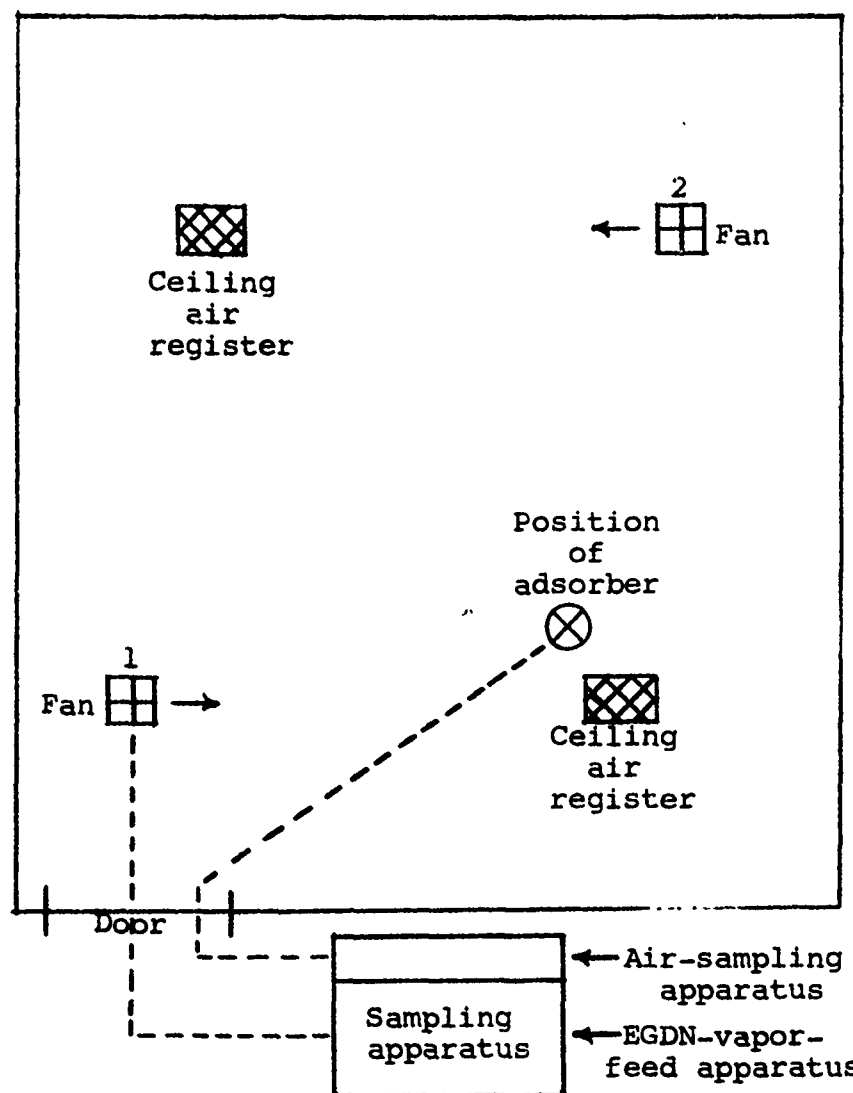


FIGURE 71 - Arrangement of 3500-Ft³ (100,000-Liter) Room

Two large electric fans rapidly stirred the air in the room. During the experiments, the air registers in the ceiling were closed so that no fresh air was fed into the room. A device for delivering measured quantities of nitrogen saturated with EGDN vapor was placed outside the room. For example, introduction of 1 liter into the room resulted in a calculated dilution factor of 100,000. This gas was introduced into the room by means of 1/8-in. Teflon tubing terminating in front of one of the fans at the grille.

The vapor feed device is shown in Figure 72. It consisted of a nitrogen gas cylinder, a flowmeter, adjustment valves, and a metal tube packed with loose dynamite granules prepared from a dynamite stick (Gelamite-II).

The air sampling from the room was accomplished by pulling air through the 340-cm²-area primary gold adsorber. The adsorber was placed 1 ft above the floor in the position indicated in Figure 71. Suction was accomplished by a small electromechanical pump located outside the room and connected to the adsorber through a 1/8-in. Teflon tubing as shown in Figure 72. The suction rate was measured with a flowmeter at the pump and was 0.5 liters/min. In each sampling, 1 to 10 liters of air was sucked through the adsorber. The adsorber was at room temperature. The sample of EGDN caught in the adsorber was transferred to the secondary adsorber and then analyzed.

Many experiments were conducted on EGDN vapor detection from the air in the room. Dilutions by factors of 10,000 and 100,000 (corresponding to 10 liters and 1 liter of dynamite-saturated vapor in a 100,000 liter room) were definitely detectable. After overnight venting of the room, good blanks were obtained. Four positive tests were conducted at each of the above dilution levels. At a dilution of 1:1,000,000, several peaks were detected but could not be clearly identified. The experimental parameters for two typical runs are given in Table XVII.

4.3 Valved Bench Apparatus

To obtain approximate retention times of EGDN in the partition columns of the engineering model and to pretest the performance of the Teflon solenoid valves on EGDN vapors during the analysis sequence, experiments were conducted in the bench-scale apparatus. Two series were run: one with the bench apparatus with pinchcocks as the valve substitutes and another with the solenoid-operated Teflon valves shown in Figure 73.

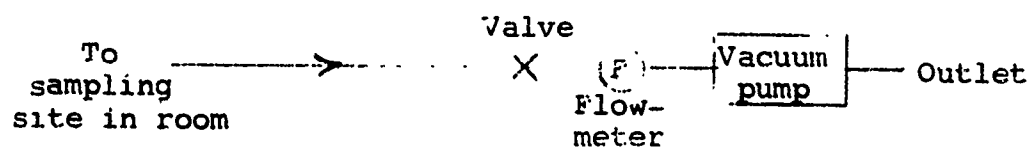
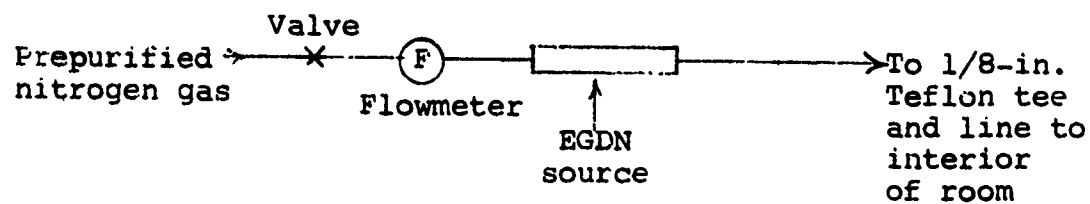


FIGURE 72 - Apparatus for Introduction of EGDN Vapors into a Room and Air Sampling from the Room

TABLE XVII - Typical Parameters for EGDN Sampling
from 3500-Ft³ Room

<u>1:100,000 Dilution</u>	<u>1:10,000 Dilution</u>
Column temp. 80°C	Column temp. 80°C
Standing current 3×10^{-8} amp	Standing current 3×10^{-8} amp
Room contaminated with 1 liter EGDN vapors at 100 cc/min for 10 min	Room contaminated with 10 liters EGDN vapors at 500 cc/min for 20 min
Vapors collected on primary adsorber at 0.5 liters/min for 2 min	Vapors collected on primary adsorber at 0.5 liters/min for 2 min
Transferred to secondary adsorber at 150 cc/min for 2 min	Transferred to secondary adsorber at 150 cc/min for 2 min
Carrier argon flow at 30 cc/min	Carrier argon flow at 30 cc/min
Positive signal with reten- tion time approximately 1.3 min	Positive signal with reten- tion time approximately 1.4 min

EGDN vapor was injected with a needle into a heated septum and absorbed in the 3-in. gold tube secondary adsorber kept in crushed ice. The adsorbed vapor was released by appropriate valving operations and by heating the secondary adsorber to 80°C. The partition columns were 10% Apiezon-L on Fluoropak 80 in 1/8-in. Teflon tubing. In the first series, the electron-capture detector was at the partition column temperature. In the second series (with solenoid valves), the detector was in a separate heating block at 135°C. The partition column temperature was 80 to 90°C.

The system used two argon supplies. One was used to maintain constant flow through the partition column; the other was used to transfer vapors from the injection port to the secondary adsorber. All valves and tubes were kept at 80 to 90°C to prevent adsorption of EGDN vapors. All the argon was cryogenically cleaned.

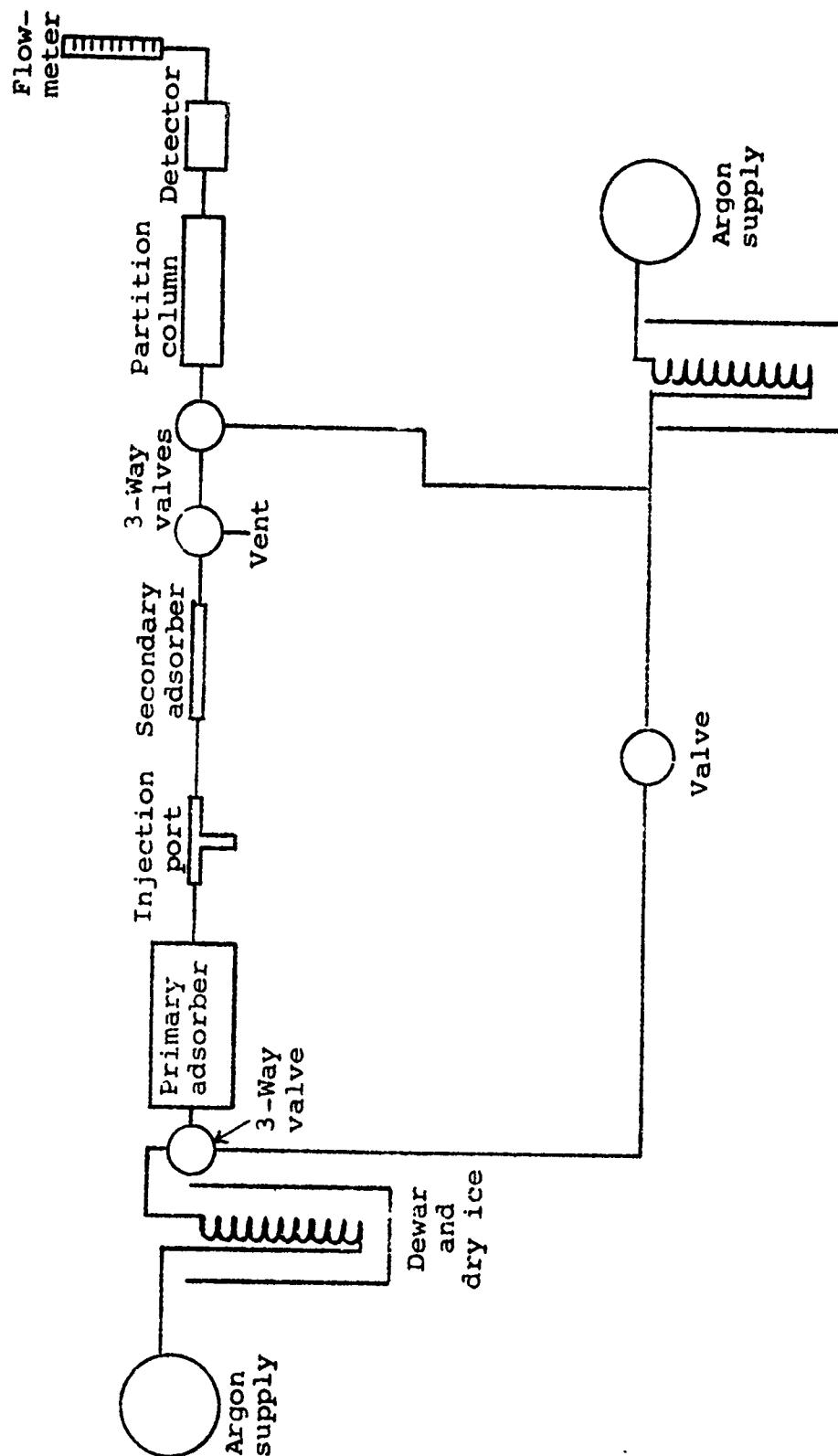


FIGURE 73 - Bench Apparatus with Solenoid Valves

The valves were connected in such a manner that the pure argon flow was maintained through the partition column at all times other than during an injection. During an injection, the flow was rerouted through the small gold tube, so that the sample could be carried on through to the column and finally through the detector.

The typical sequence for the tests with solenoid valves was as follows.

- (1) Valves were in the nonenergized (closed) position. The argon flow bypassed the secondary adsorber and went directly through the column and the detector.
- (2) The temperature of the secondary adsorber was reduced to 0°C.
- (3) The injection needle with EGDN was placed in the injection port.
- (4) A second argon supply was used to adjust the flow to 150 to 200 cc/min for 5 min for transfer. The secondary adsorber was heated to 80°C.
- (5) The valves were opened for the desired injection period.
- (6) The chart paper was marked accordingly, indicating the beginning of sample injection and the resulting retention time.

Representative data are shown in Table XVIII. The weight of the Apiezon-L/Fluoropak packing was 0.404 g in the first series and 0.700 g in the second.

The data indicated that reasonable retention times, on the order of 1 min, can be obtained in the geometry and the mode of operation closely resembling those of the engineering model. An argon flow rate of 20 to 40 cc/min, a partition column temperature of 80 to 90°C, a detector temperature of 140°C, and a Teflon solenoid valve temperature above 80°C gave satisfactory performance.

With the solenoid valves, it was possible to obtain a stable base line and accurate injections of vapor from the secondary adsorber into the analytical section. In comparison with the pinchcock operation, the solenoid valves minimized flow disturbances; i.e., the usual pressure spike

observed during the beginning of vapor injection from the secondary adsorber was minimized.

The overall experience was that the retention times were reproducible within 10% and that very good separation of the EGDN and nitrobenzene peaks was achieved.

TABLE XVIII - Retention Times in Valved Bench-Scale Apparatus

<u>Valving</u>	<u>Flow Rate, cc/min</u>	<u>Retention, Time, min</u>	<u>Column Temp., °C</u>	<u>Block Temp., °C</u>	<u>Standing Current, amp</u>
Pinchcocks	15	1.50	90	137	2.8×10^{-8}
	21	1.38	90	140	2.9×10^{-8}
	27	0.95	82	140	2.6×10^{-8}
	34	0.75	82	140	2.6×10^{-8}
	44	0.56	82	140	2.6×10^{-8}
Teflon solenoid	20	1	80	140	2.8×10^{-8}
	22	1.2	80	140	2.8×10^{-8}
	35	0.9	90	140	2.7×10^{-8}

This fixed-adsorber system with heated connections eliminated many disturbing effects that were observed in the previous system, and more accurate EGDN detection became possible. Figure 70 shows two typical EGDN peaks recorded with the improved apparatus.

4.4 Design of Engineering Model

This section is written as a complete unit that can be understood without reference to the preceding material.

The bomb detector, designed as an engineering model for experiments on detection of dynamite under realistic conditions, consists of a primary adsorber, a secondary adsorber, a partition column, an electron-capture detector, and electronic circuits.

Dynamites evolve vapors of ethylene glycol dinitrate (EGDN), and the bomb detection is based on detection of this chemical in air in which it is present as a dilute vapor.

The primary adsorber, through which air is passed at a high rate and at ambient temperature, adsorbs EGDN molecules on its gold surface. After the air sampling, the EGDN is transferred by a stream of clean argon to a much smaller, secondary adsorber with a gold surface. During the transfer, the primary adsorber is at 80°C and the secondary adsorber at 0°C.

For analysis, EGDN is desorbed from the secondary adsorber at 80°C and flushed through the partition column toward the detector. The partition column is packed with shreds of Apiezon/Fluoropak, and its function is to delay the passage of EGDN for a controlled period of time. This interval, from the heating of the secondary adsorber to the response of the detector, serves as a partial identifier of EGDN. The detector signals the arrival of EGDN by a decrease in ionic current. The electronic circuit transfers the change in the electrical current flow through the detector into a recordable readout and can transform it into any other form of signal (bulb, bell).

Thus, to be identified as EGDN, the vapor must adsorb on gold at ambient temperature, desorb at 80°C, spend a certain characteristic time interval (on the order of 1 min) in the partition column, and produce a response in the electron-capture detector. Every one of these requirements separately can be met by many compounds in vapor form, but together they very severely limit the probability of a "false" reading, since it is very difficult for some other substance to meet all four requirements. For further limitation, additional requirements could be introduced if necessary.

The development of the concepts, design details, and modes of operation is described below.

The earlier work showed that polar vapors are attracted to metals and are adsorbed rather strongly on metal surfaces. EGDN is a polar molecule* and a strong electron acceptor, and

* Polar molecules are those in which the center of all negative charges (electrons) do not coincide with the center of all positive charges. Examples: In water, $\text{H}^-\text{O}-\text{H}^+$, the negative charges are located near the oxygen, but the positive charges are closer to the hydrogen.

it is capable of being adsorbed onto a metal surface. The vapors can be desorbed from the surface by heating to a suitable temperature. Because of this behavior, it became necessary to use a material other than the gold tubes, onto which there would be as little adsorption as possible. Teflon was chosen as the most suitable material. Thus, the entire vapor sampling device, transport lines, valves, connections, and chromatographic column are constructed of Teflon. The gold tubes constitute the only metal internal to the device.

Sampling of air is achieved with the primary vapor collecting device shown in Figure 74. Air is drawn into the housing and over three concentric seam-welded gold tubes by two Globe blowers in tandem. Figure 75 shows the wiring schematic, the blower, and the primary closure motor. The total surface area of gold available for adsorption is 364 in.². Turbulent flow is achieved by using an airflow rate of 200 cfm and channeling the flow through 108.25-diameter holes in a 4.75-diameter retainer.

The gold tubes are heated by electrical induction. Each gold tube acts as a one-turn short in a transformer. The heat from the electrical induction causes the EGDN to desorb from the gold surfaces. Since desorption must be uniform and complete, without overheating of one tube or underheating of another, it became necessary to adjust the thickness of the foils so that they all have the same electrical resistance. Initially, copper models were fabricated and thermocouples were fastened to each tube. Power was applied to the inductor, and when the temperature of the tubes reached equilibrium in the closed system, temperature readings were made.

The middle tube was calculated to be 6.6 mils thick and outside tube 8.4 mils thick, based on the resistivity of gold, a center tube thickness of 5.0 mils, and:

$$\frac{P_1}{P_2} = \frac{R_2}{5R_1}$$

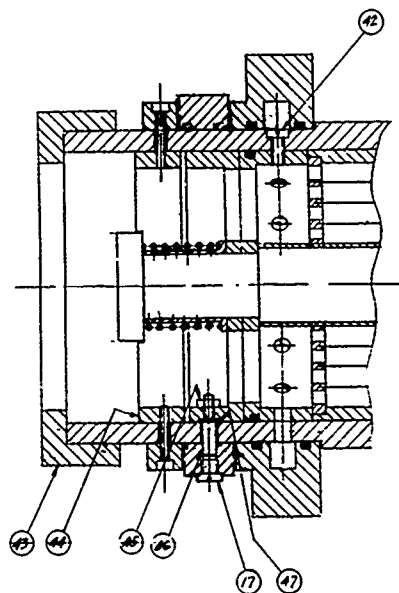
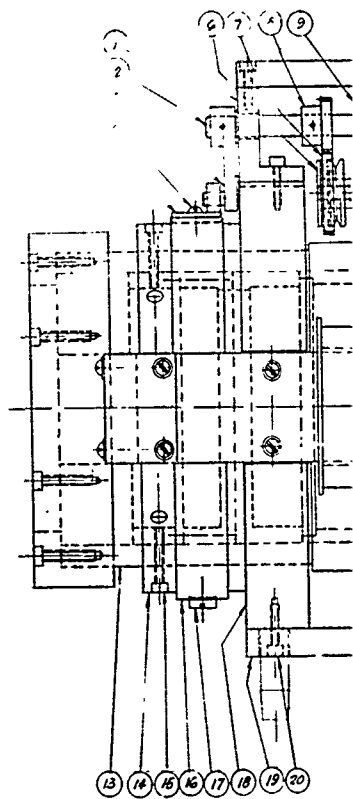
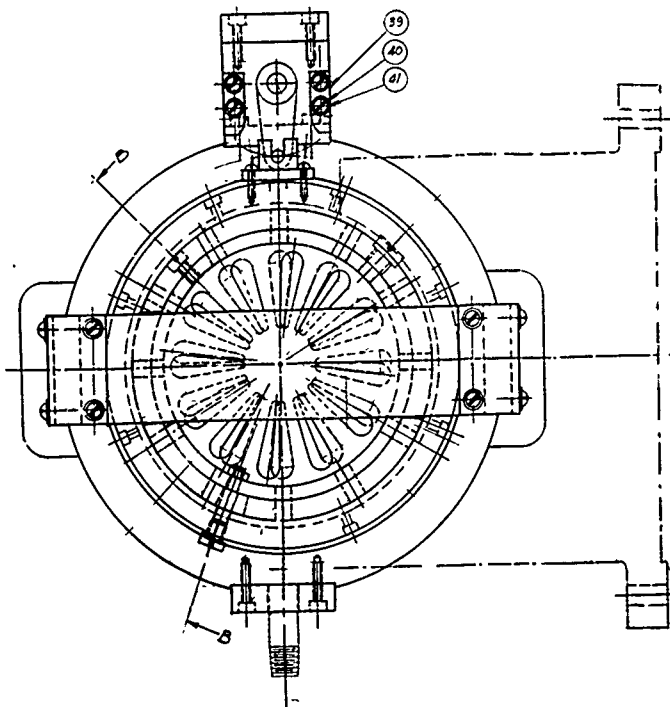
P_1 = T above room temperature for 5.0-mil tube

P_2 = T for middle and outside tubes

R_1 = diameter of inside tube times thickness (in mils)

R_2 = unknown thickness (in mils) times known diameter.

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SECTION B-B

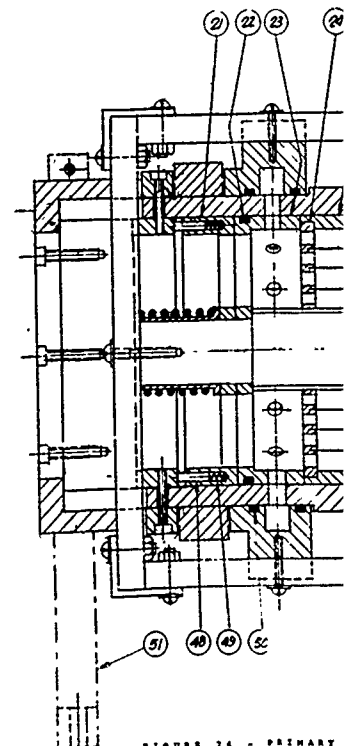


FIGURE 74 - PRIMARY

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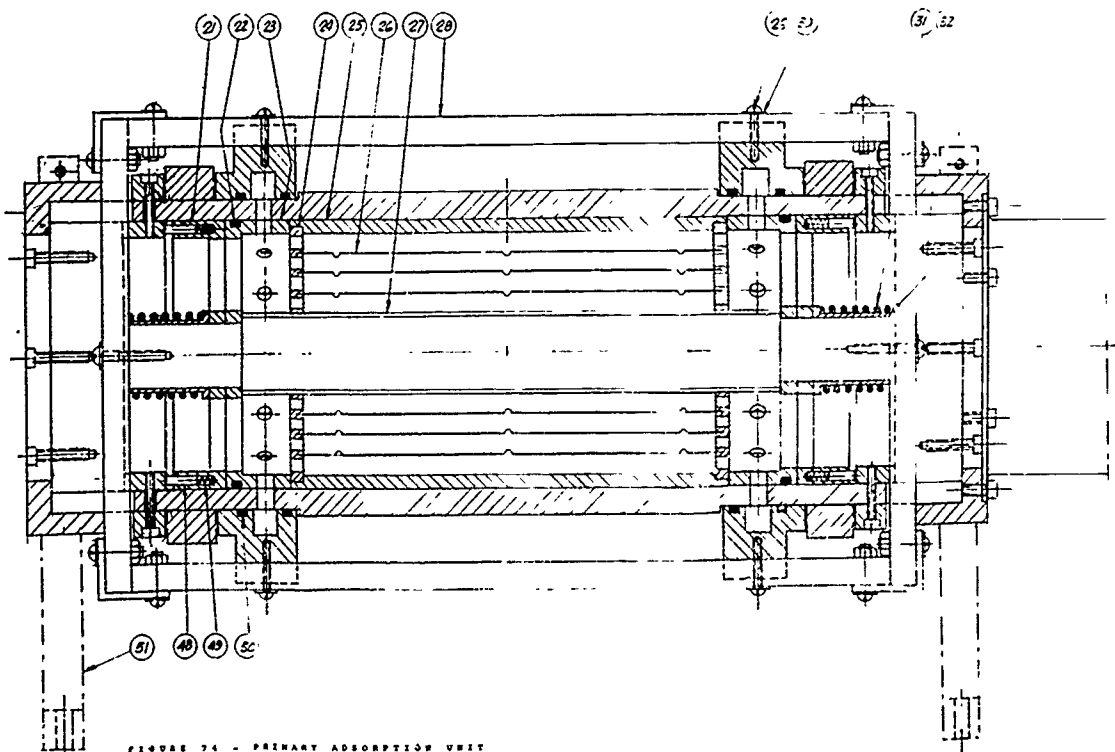
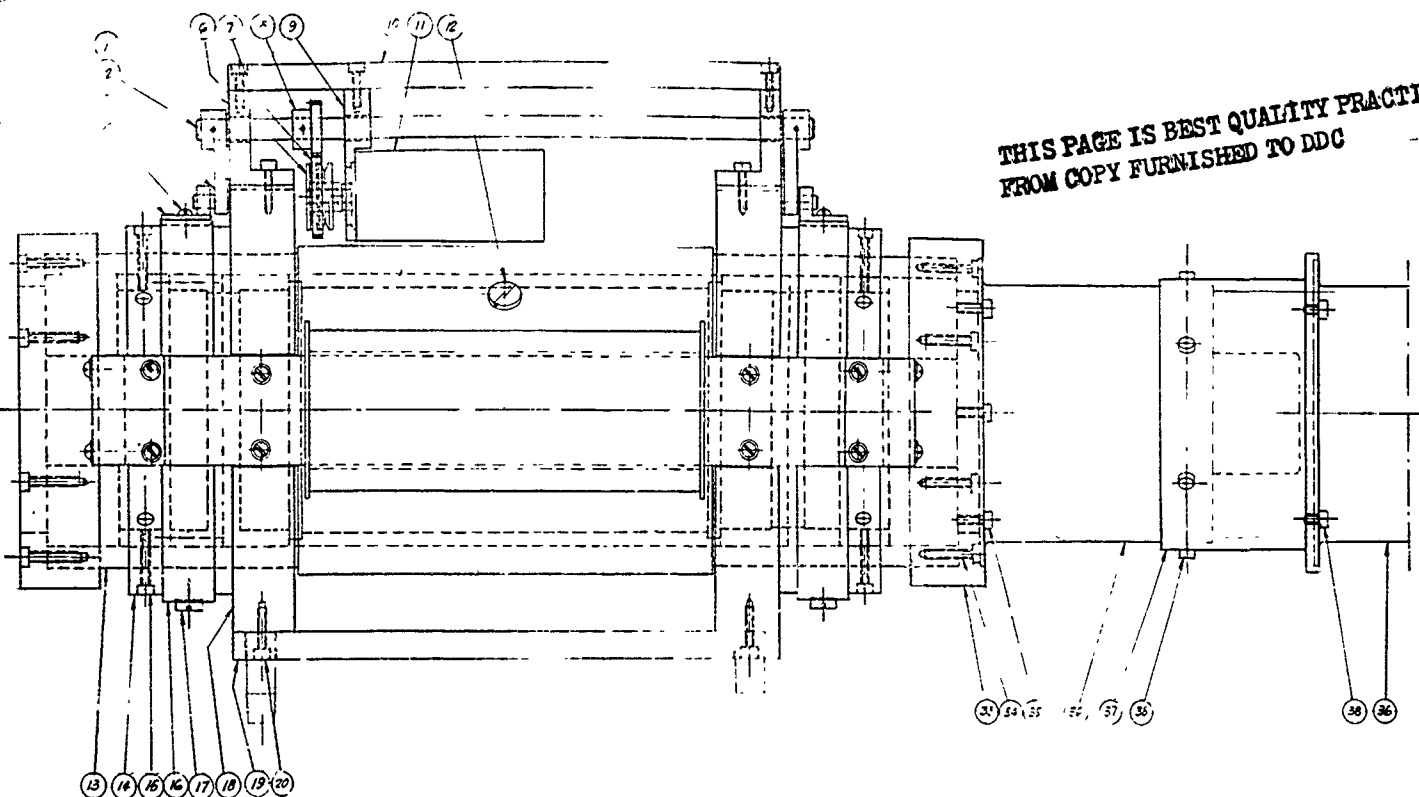


FIGURE 74 - PRIMARY ABSORPTION UNIT

ITEM NO.	DESCRIPTION	QTY
1	FLANGE ALUMINUM	1
2	FLANGE ALUMINUM	1
3	FLANGE ALUMINUM	1
4	FLANGE ALUMINUM	1
5	FLANGE ALUMINUM	1
6	FLANGE ALUMINUM	1
7	FLANGE ALUMINUM	1
8	FLANGE ALUMINUM	1
9	FLANGE ALUMINUM	1
10	FLANGE ALUMINUM	1
11	FLANGE ALUMINUM	1
12	FLANGE ALUMINUM	1
13	FLANGE ALUMINUM	1
14	FLANGE ALUMINUM	1
15	FLANGE ALUMINUM	1
16	FLANGE ALUMINUM	1
17	FLANGE ALUMINUM	1
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33	FLANGE ALUMINUM	1
34	FLANGE ALUMINUM	1
35	FLANGE ALUMINUM	1
36	FLANGE ALUMINUM	1
37	FLANGE ALUMINUM	1
38	FLANGE ALUMINUM	1

117 RESEARCH INSTITUTE
TECHNOLOGY CENTER
PRIMARY ABSORPTION COLUMN
KRA, BOMB DETECTOR

SCALE: 1/4" = 1" (SEE NOTE)
FULL SCALE: 1/4" = 1" (SEE NOTE)
PART NO: C-6055-1

NOTE: ALL SCREWS AND NUTS TO BE
STAINLESS STEEL UNLESS OTHERWISE
SPECIFIED

2

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MS 3106A125-3P

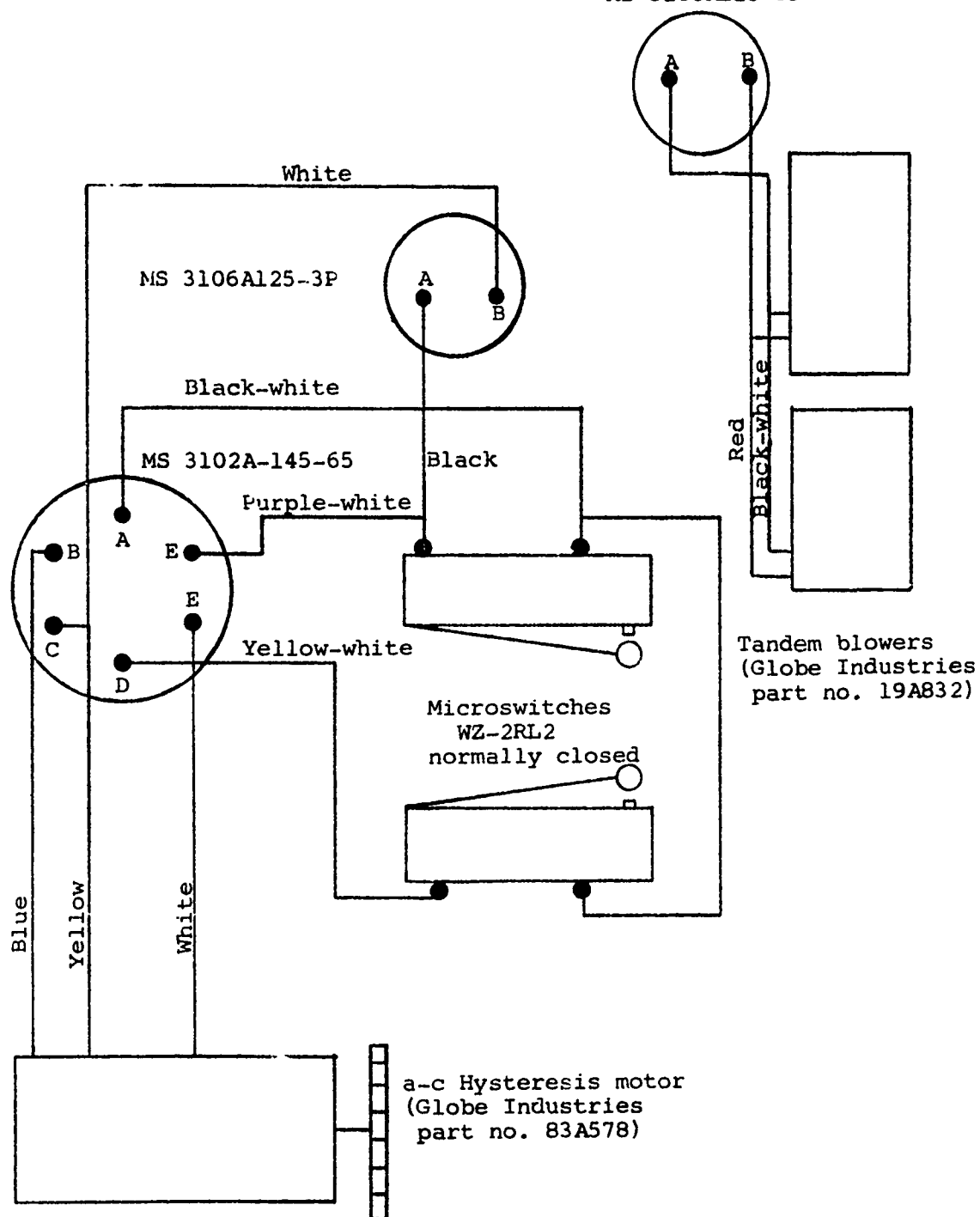


FIGURE 75 - Motor-Blower

After fabrication, the tubes were tested and the results were: inside, 54°C; middle, 55°C; and outside, 45°C. These readings were taken after 3.5 min at 2.5 amp and 44.5 v. Heat losses to the Teflon housing are responsible for the lower temperature of the outside tube.

During sampling, the inlet and exhaust ports are opened. When sampling is completed, the ports close and electrical induction begins. During this time, a valve is opened and argon is allowed to enter the sampling chamber. The argon enters at the rear of the chamber through a distribution collar at a rate of 8 liters/min. A manifold of this type is required to provide thorough flushing of the gold surfaces.

After the argon has passed over the gold surfaces and has carried the EGDN vapors with it, it leaves the chamber via the forward manifold and is transferred through a series of Teflon valves and tubes to the secondary adsorber, where the vapors are adsorbed for a second time. The secondary adsorption unit is shown in Figure 76. Next, the primary unit is "baked out" by raising the temperature of the three gold tubes to approximately 150°C. This higher temperature decomposes any residual vapors, so that the unit is clean for the next sampling. This bakeout mode is continued throughout the rest of the cycle.

While the sample is being transferred from the primary unit to the secondary adsorber, a Rauge-Hilsch vortex tube is activated to cool the secondary tube to 0°C. This ensures complete adsorption of EGDN vapors. The vortex tube is a small instrument that converts compressed air into hot and cold air. There are no moving parts. The air enters holes that inject it tangentially. This creates a cyclone spinning at 1,000,000 rpm. The center of this vortex is cold air that flows out through a hole in the bottom of the tube. The hot air leaves from the top of the tube. Essentially, the vortex tube is a simplified radial in-flow turbine capable of cooling the gold tube to 0°C.

After the vapors have been adsorbed on the secondary adsorber, a 10-v potential is applied to a 1-ohm resistance Nichrome wire wrapped around the gold tube inside the unit. The wire is insulated with asbestos. A thermocouple, however, is in intimate contact with the gold tube, and the temperature is controlled at $80 \pm 5^\circ\text{C}$. The temperature increases from 0 to 80°C in 45 sec. After the desired temperature is reached, a valve is opened, and the vapors are carried on through to the chromatographic column for a specific period.

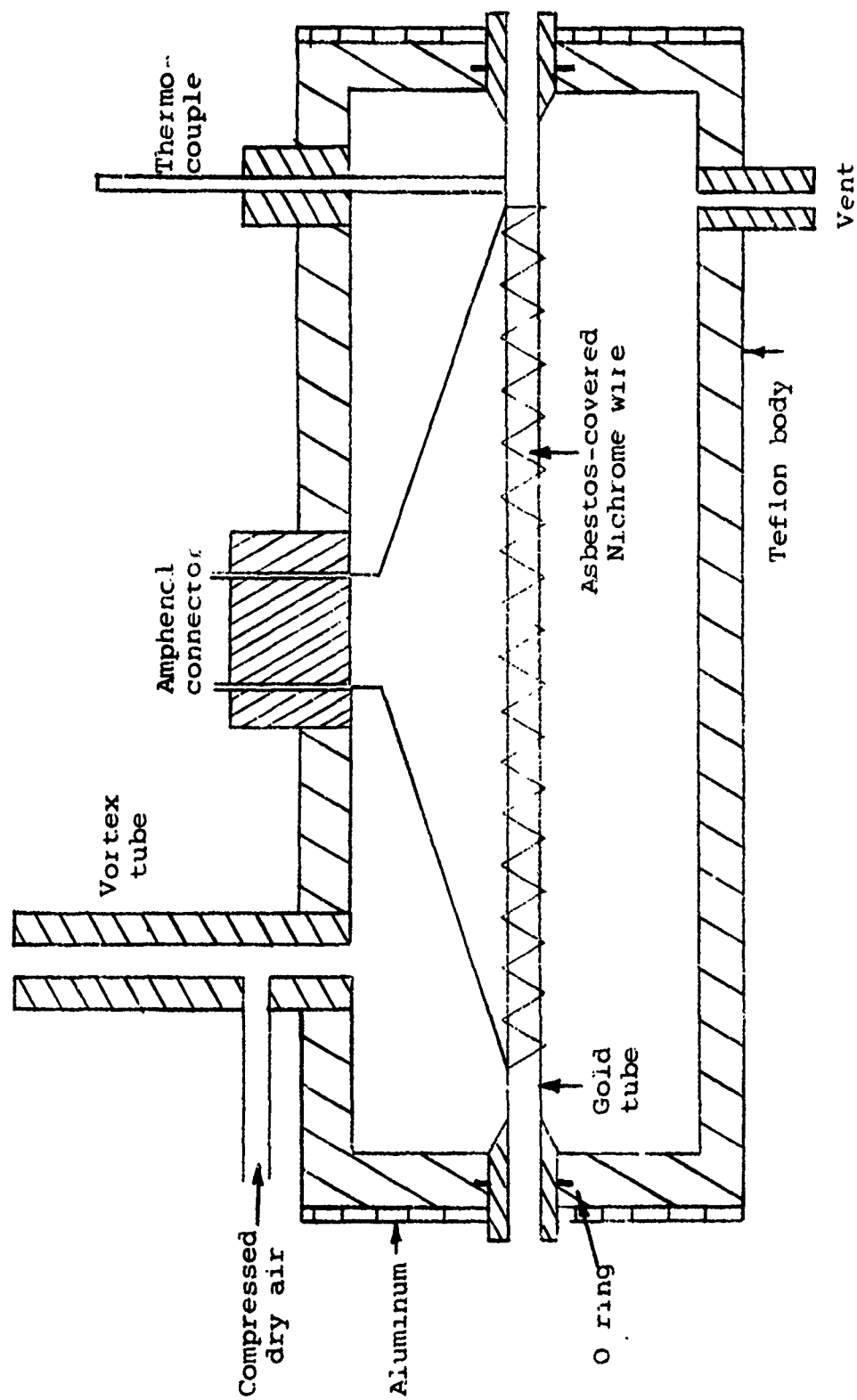


FIGURE 76 - Secondary Adsorption Unit

This valve closes after the injection and thus traps the balance of the sample for verification.

When the sample is injected into the chromatographic column, another valve opens to continue the flow past the electron detector. The chromatographic column contains 0.690 g of 10% Apiezon-L on Fluoropak 80 (from the Wilkens Instrument Co.). The function of the column is to separate complex mixtures of organic substances. The column is in a thermostatically controlled copper block oven controlled to about $\pm 0.1^{\circ}\text{C}$ by a time-proportioning pyrometer.

When EGDN vapors are injected into the column, they pass over the Apiezon-L coated packing. Since EGDN vapors are soluble in the liquid phase, they come to equilibrium with it. The carrier gas (argon) gradually washes the vapors, through a repeated process of vaporization and solution, down through the column. As the carrier gas sweeps over the stationary Apiezon-L film phase, some of the vapors are released into the gas phase in a reversible dynamic equilibrium. Finally, the vapors emerge from the end of the column and enter the electron-capture detector.

Because of this equilibrium process, materials of different volatility are separated in both space and time. Highly volatile gases and inert gases emerge very rapidly from the column. Depending on their particular characteristics, less volatile materials are retained for longer periods.

At a flow rate of 50 cc/min and a column temperature of 90°C , the retention time for pure EGDN is 1 min and 30 sec. Previous experiments indicated that these are desirable operating conditions. Normally, gas is passed in the forward direction for about 3.5 min. At all other times flow is in the reverse direction; this cleans the detector of all vapors with a low vapor pressure. This material backwashes out a vent valve and not through the forward transport system. By prolonged backwashing from a clean argon supply, the electron-capture device can be maintained at optimum operating efficiency. When the electrodes are contaminated with heavy vapors, the operating efficiency is drastically reduced. Essentially constant backwashing keeps the detector clean.

Vapors leaving the partition column enter another copper block oven containing the electron-capture detector at 140°C . The temperature of this unit is maintained by another time proportioning module. The electron-capture detector was chosen for development over the other methods of detection because it is several orders of magnitude more sensitive to the type of molecule to be detected and is not disturbed

by hydrocarbons that are encountered in airport and airplane air. The detector becomes an active element in an electronic circuit -- somewhat like an amplifier tube in a radio circuit.

This electron-capture detector is essentially an ionization device. Ordinarily, gases are very poor conductors of electricity, and some means of introducing ions between the anode and the cathode of the detector to allow a current to flow between them is necessary. This is accomplished by a foil of titanium metal that has been reacted with the radioactive hydrogen isotope, tritium, the source of high-energy electrons called "beta particles." These interact with the carrier gas atoms to form positive ions and lower-energy slow electrons. Under the electrical potential of the battery, collection of these electrons at the positive anode and the inlet tube causes a current to flow through the input resistor of an electrometer or d-c amplifier.

When any material that is capable of forming stable negative ions enter the detector, some of the electrons flow toward the anode and react to form such ions. Since the mobility of an anion is some 10^5 or 10^6 times less than that of the free electrons, the anions are carried away by the flowing carrier gas molecules rather than being discharged at the anode. Hence, the current flowing through the input resistor is greatly reduced, and the signal is easily amplified and measured.

Upon completion of the detection sequence, another sample can be injected into the column if the operator so desires. However, if he desired to start another sampling cycle, the secondary adsorber must be backed out. This is an extremely important step and has automatically been incorporated into the electronics. The electronics wiring schematic and the cable schematic diagrams are shown in Figure 77 and 78, respectively. During bakeout, the temperature of the secondary gold tube is increased to 150°C and is controlled by the same pyrometer that regulates the 80°C desorption temperature. After bakeout is complete, the apparatus is ready for another complete cycle.

It was found that at room temperature a measurable amount of EGDN adsorbs on the Teflon parts. To reduce the adsorption to a minimum, all Teflon tubing and valves were placed in ovens maintained at 74 to 80°C . The ovens were constructed of Transite board and were covered with a aluminum shell with a $3/16$ -in. air space between. The three ovens require about 40 w total and operate through snap-action thermostats. They go on when the apparatus is turned on and do not go off until the preset point is reached.

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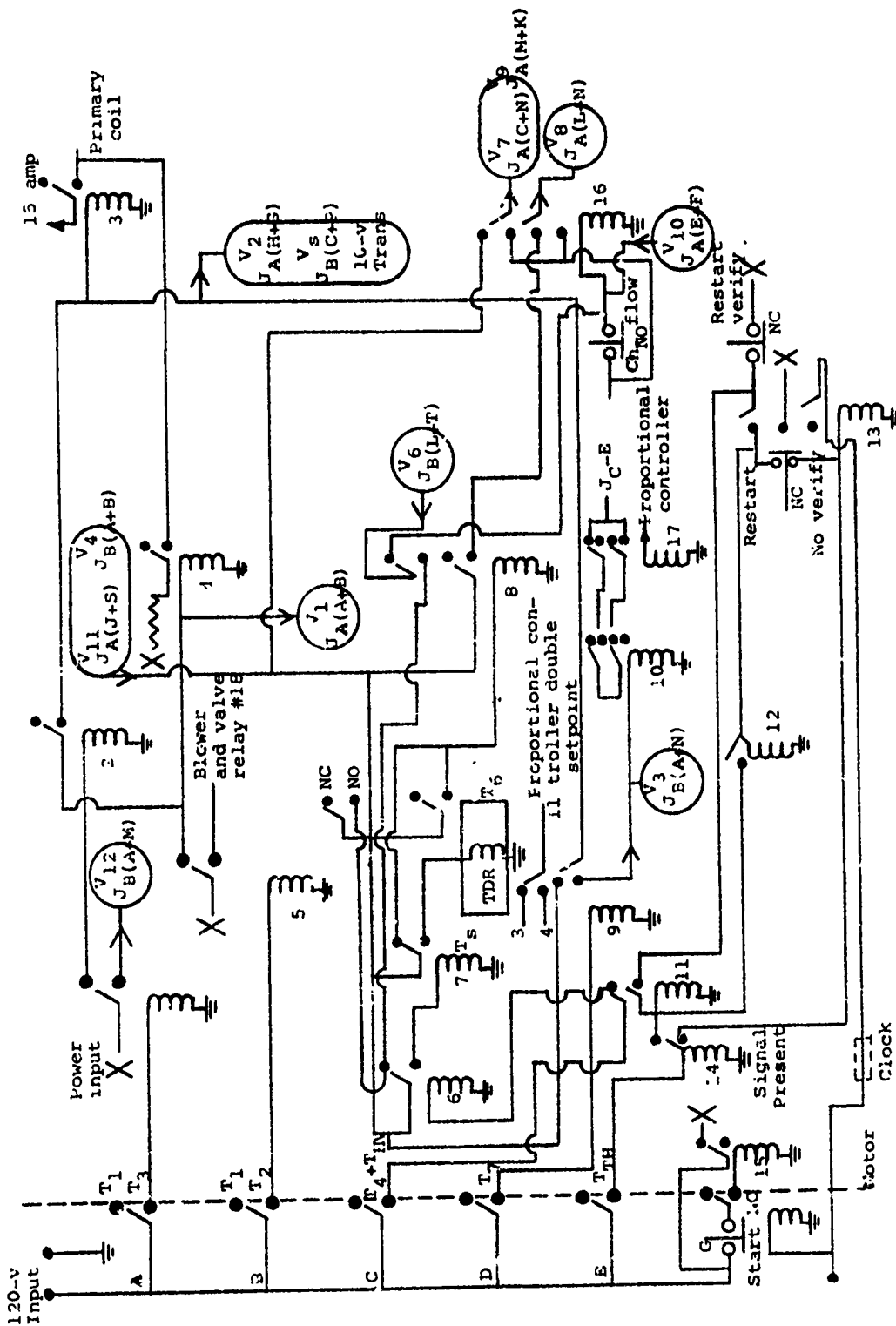
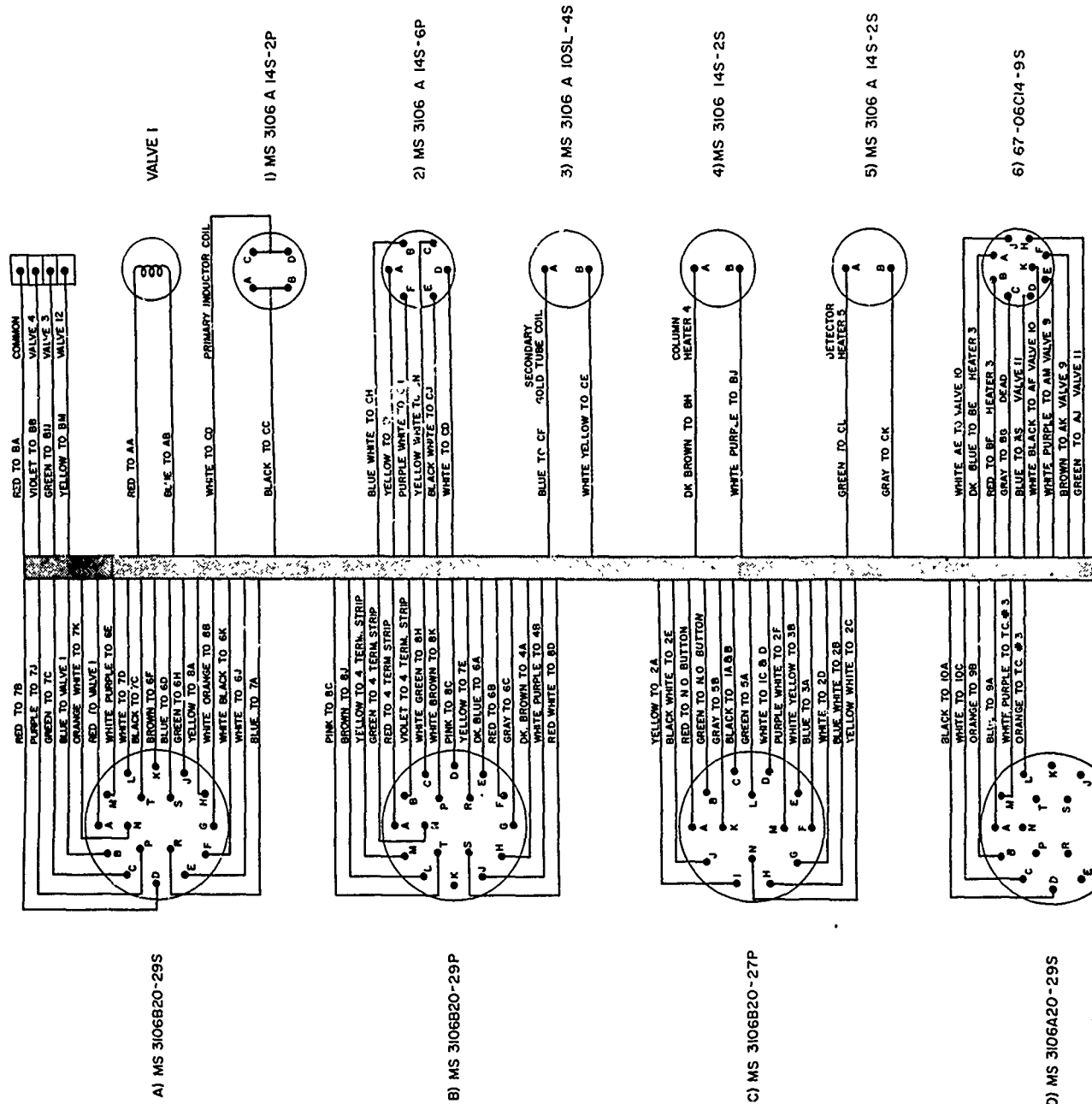


FIGURE 77 - Electronics Wiring

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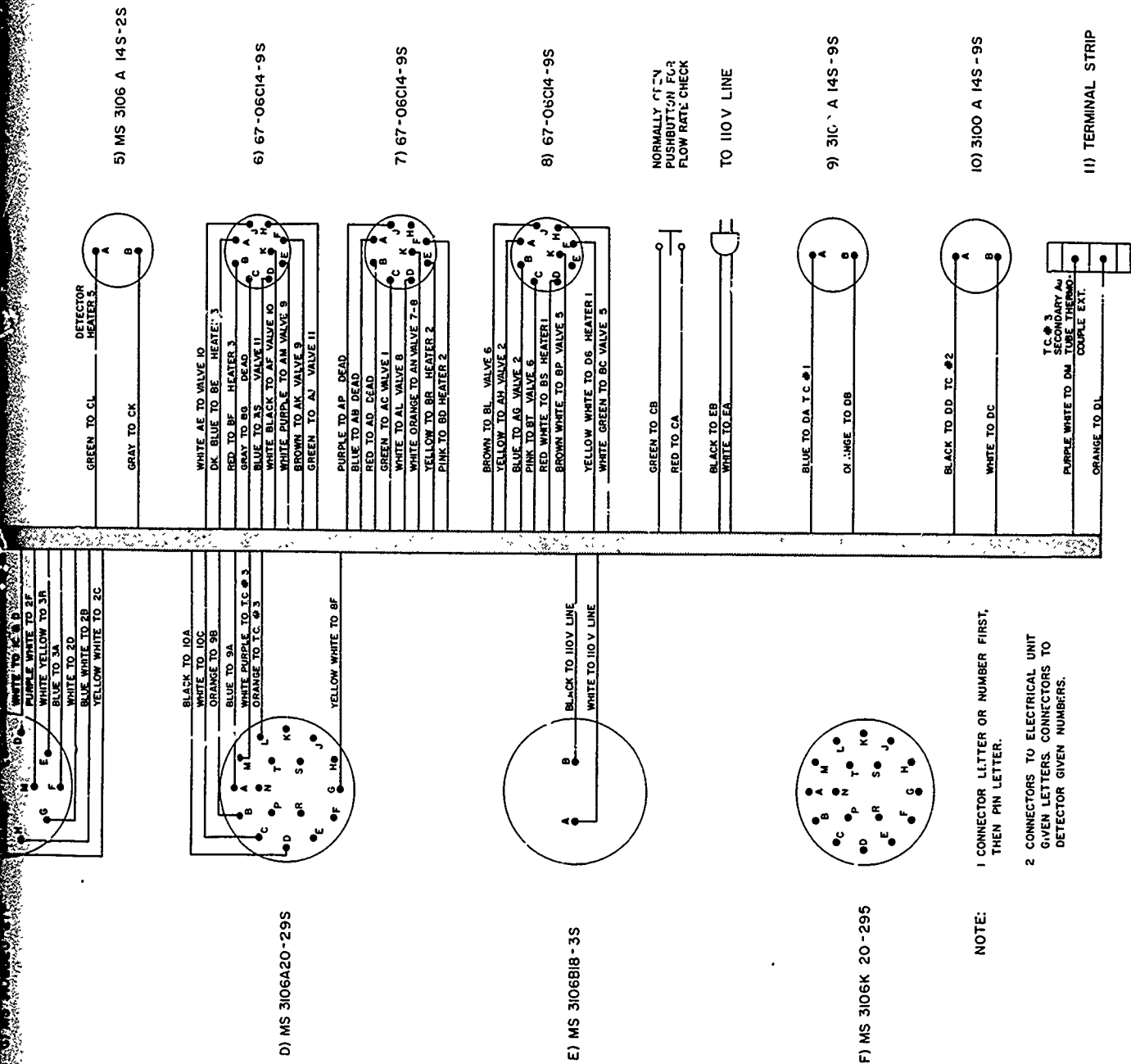


FIGURE 78 - CABLE SCHEMATIC

The wiring schematics for the three ovens are shown in Figures 79, 80, and 81, respectively.

It is necessary to control the temperature of the ovens closely so that the Teflon valves seat tightly. The valves must be adjusted at the operating temperature. Any significant temperature change causes the valves to leak.

The electron-capture device was found to be sensitive to flow changes. Thus an independent supply of argon was required for the analytical sequence. The argon used for this sequence was "zero" argon, certified to contain less than 0.5 ppm of hydrocarbon. The vapor transport system through the primary adsorber and secondary adsorber is fed with argon certified as 99.996% pure. Each argon supply is provided with a fine-particle filter system. The filters are Gelman White Metrical GM-6, with a 0.45- μ pore size, and a type E fiber-glass prefilter.

The flow system is shown in Figure 82; and the cycles of operation, as controlled by the rotary cam timer, are shown in Table XIX.

Idle position. All valves are in their normal position, which is nonenergized. Power supply to the ovens is on, and the pyrometers control the partition column and the detector. The primary adsorption unit is closed to avoid contamination. The partition column and the detector are in the backwash mode with atmospheric venting at the rate of 50 cc/min through valve 7. The forward flow rate can be checked by a pushbutton switch connected to a rotameter.

Initial sampling. (1) Start button is depressed to activate the cam timer. (2) Power is applied to valve 12, and the vortex tube begins to cool the secondary adsorber to 0°C. This continues until transfer from the primary to the secondary is complete. (3) The primary unit is opened, and the blowers are activated.

Sample transfer. (1) The above steps continue, except the primary unit closes and the blowers are turned off. (2) The primary unit inductor coil is supplied with 5 amp to heat the gold tubes to 80°C. (3) Valve 1 opens.

Secondary gold tube warm-up. The above continues, except: (1) 8 amp is supplied to the primary inductor, (2) valves 2, 11, and 4 through 9 are actuated, (3) valve 12 is deactuated, and (4) 10 v is applied to the secondary gold tube heater.

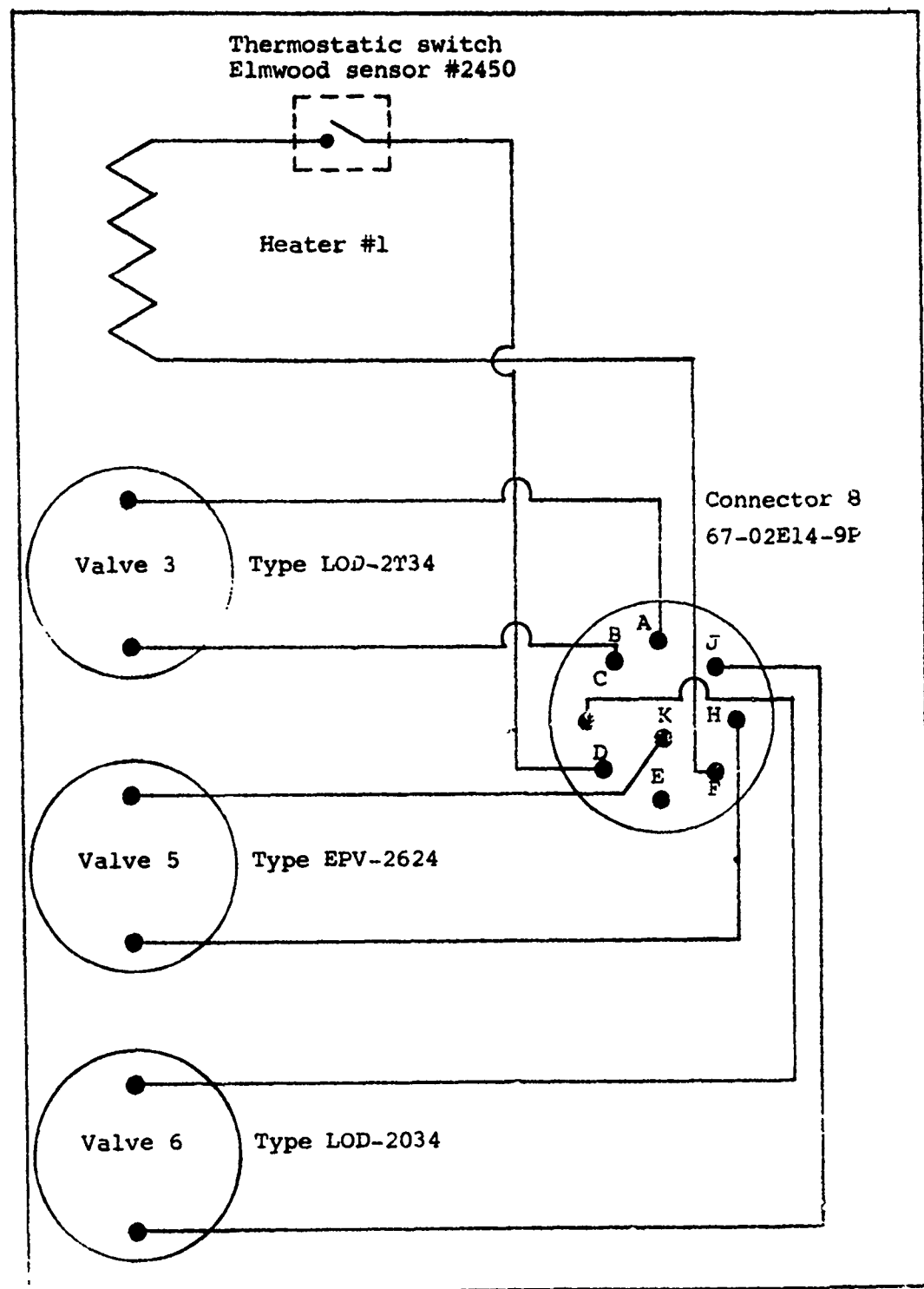


FIGURE 79 - Wiring for Oven 1

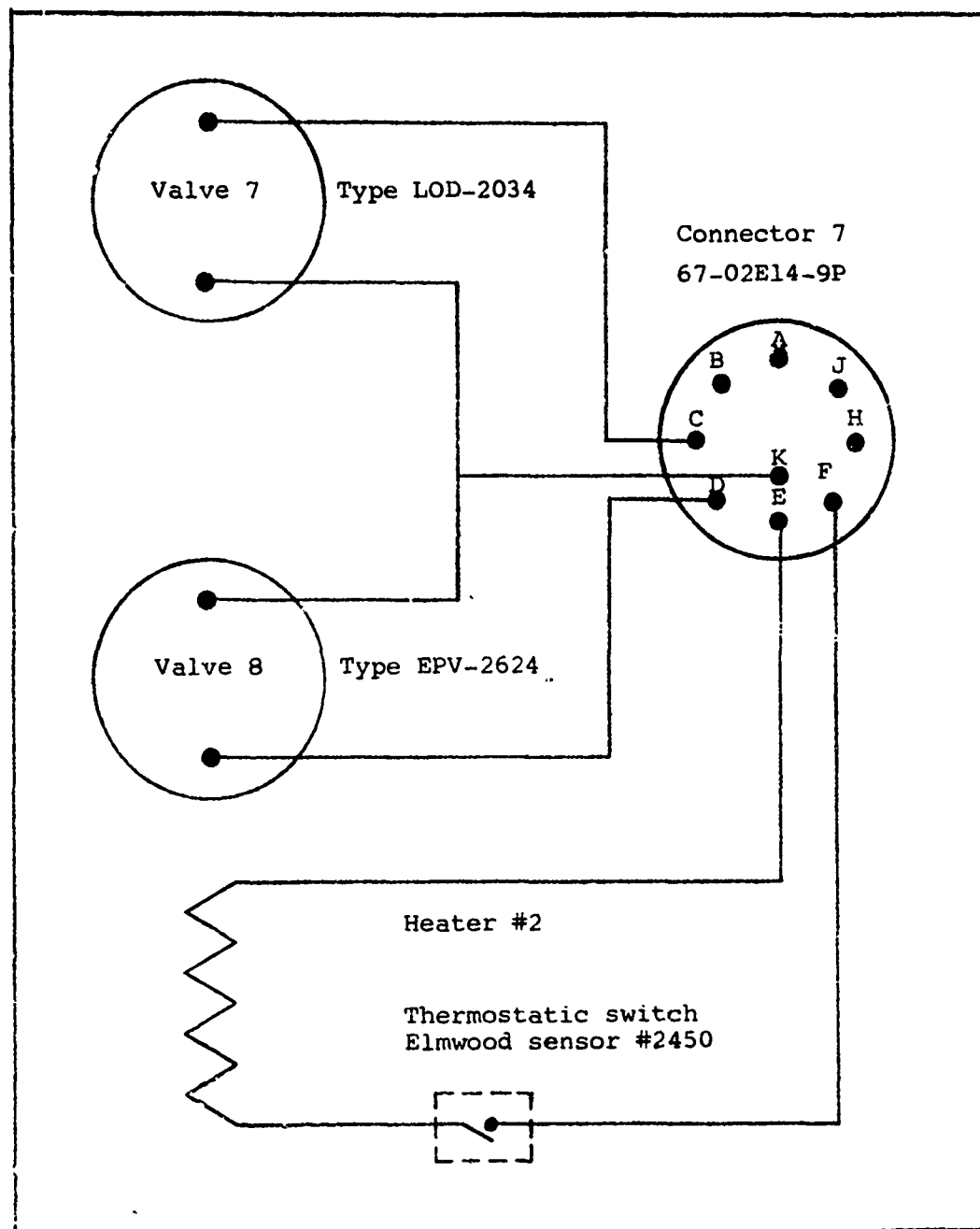


FIGURE 80 - Wiring for Oven 2

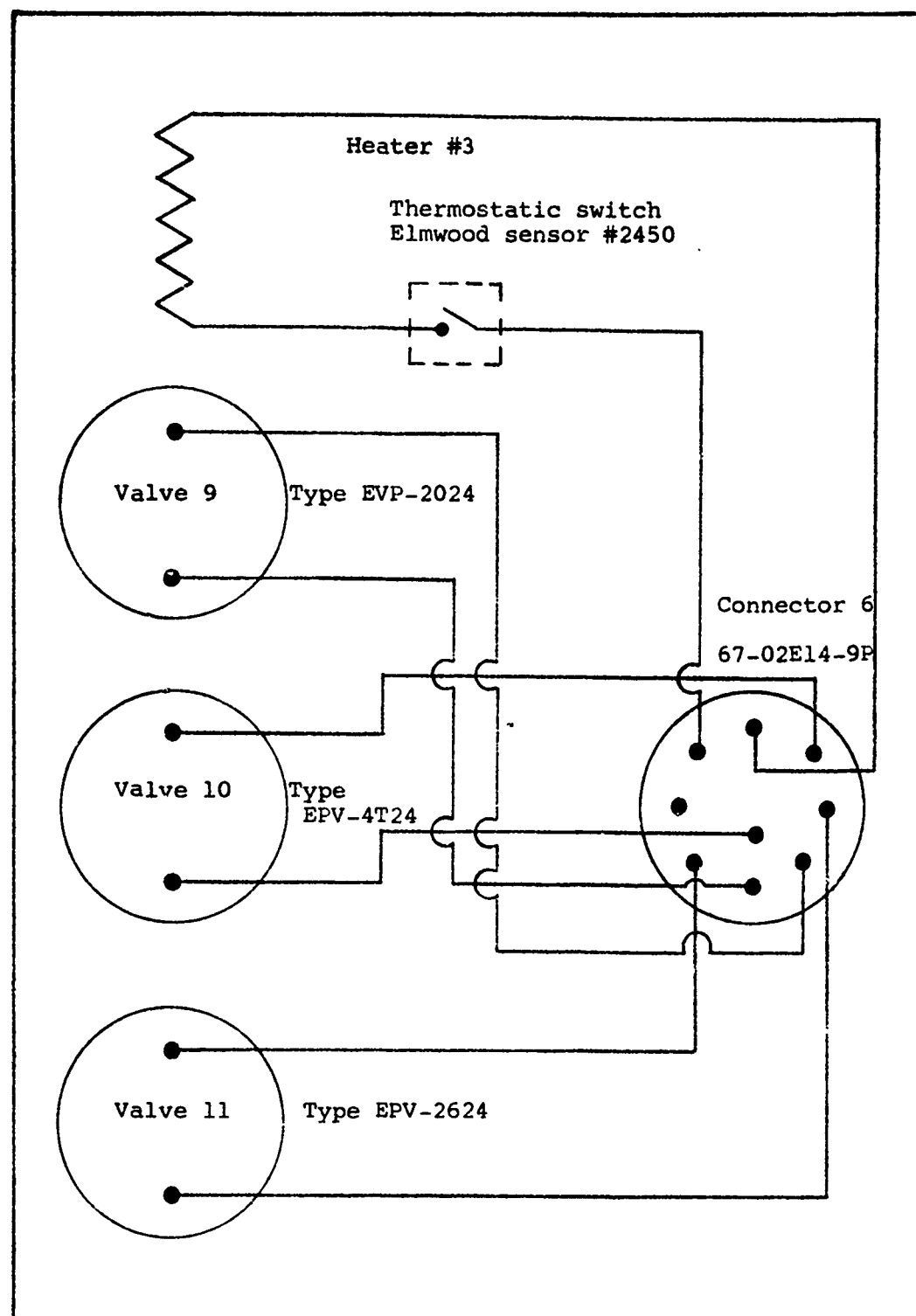


FIGURE 81 - Wiring for Oven 3

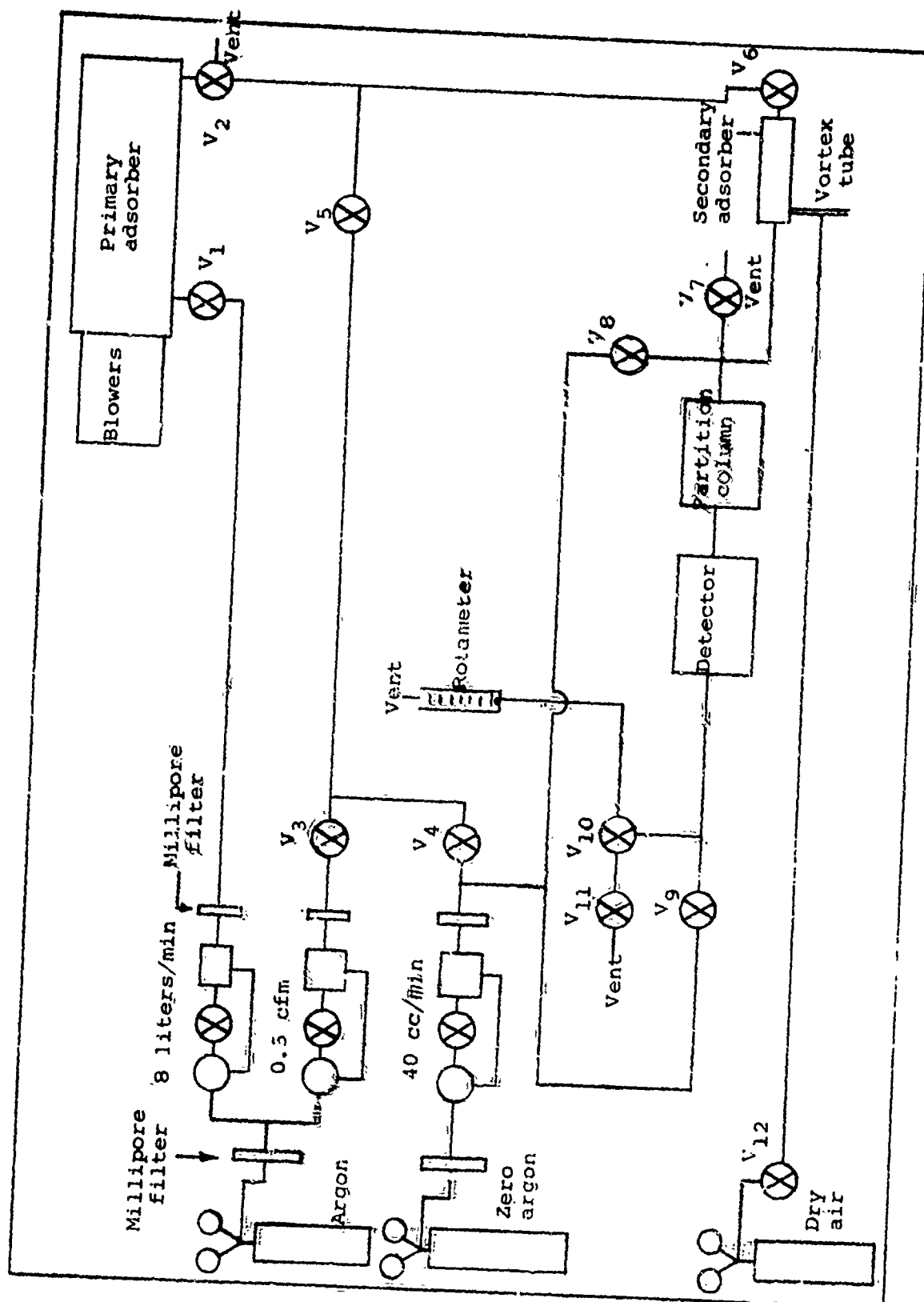


FIGURE 82 - Flow System

TABLE XIX - Position of Cam Timer versus Relays and Valves Actuated

Cam Position	Relays Actuated	Valves Actuated ^a
		1,2(3-way), 4,5,6(NO)
NO ^a	2,3,4,8,17	7(NO),8,9(NO),11
A	1,4,17	1,12
B	2,5,17,18	Blowers and primary unit caused to close
C	2,3,4,6,7,8,17, and TDR (time delay relay)	2,3(3-way),4,5,8,11
D	2,3,4,9,10	1,2,3,5
E	2,3,4,8,9,10,11,17	1,2,4,5,6(NO),7(NO),8,9(NO),11
G	15,17	

^aNO, normally open. Valves normally closed (NC) unless specified as NO or 3-way valve.

Sample injection and development. (1) The above continues. (2) The variable time delay (TDR) relay is actuated (1 to 30 sec) and causes valves 6 and 8 to open and close, respectively. (3) The time delay relay returns to normal position and causes valves 6 and 8 to close and open, respectively. (4) The sample continues to flow through the chromatographic column toward the detector. (5) The remainder of the sample not injected from the secondary gold tube is retained at 80°C.

Verify (optional). (1) If a signal is present, a red light appears on the control panel and the cam timer stops. (2) The operator has the option to continue toward bakeout of the secondary gold tube or to inject another sample to verify the first signal. (3) If restart and no verify is decided upon, the button marked "Restart and No Verify" is pushed. (4) If verify is desired, the button marked "Verify" is pushed. (4a) The cam timer restarts and injects another sample from the secondary gold tube. (4b) If a signal is present, a light appears and the cam timer stops.

Bakeout secondary adsorber. (1) Valves 1, 2, 3, and 5 are still energized. (2) Valves 4, 6, 7, 8, 9, and 11 are de-energized. (3) The secondary gold tube is heated to 150°C and controlled by the pyrometer. (4) The primary adsorber is still baking out.

Stop. Return to idle mode.

The timing sequence can be reset to fit any desired time. The cam timer speed is determined by a motor drive, which is easily replaced with others of different speeds. The present cam speed is one complete revolution per 10 min. Teflon actuators placed into slots on the cam can close the relay contacts mounted on one side of the timer. The position of the actuator in relation to the contact determines what the detector does. By placing one actuator after another around the cam, that operation time becomes 10 min. See Figures 83 and 84.

4.5 Demonstration of Engineering Model

The results obtained from the engineering model are summarized in Table XX. The transfer rate from the primary adsorber to the secondary adsorber and the transfer time in all runs were kept constant.

The first run consisted of placing an open container of dynamite at the inlet of the primary adsorber. The adsorber was then activated for 10 sec. The sample was then processed. The resulting retention time was 1.2 min, with a peak height of 80 divisions. This initial test indicated that the engineering model was capable of sampling, transferring, and detecting the explosive vapors released by dynamite.

The next run consisted of placing an open container of dynamite in a test chamber. The 3000-liter test chamber had a wooden framework enclosed by polyethylene film. The dynamite vapors were allowed to diffuse for a period of 5 min, after which the primary adsorber was activated for 1-1/2 min. The sample was then processed. The resulting retention time was 1.2 min, with a peak height of 85 divisions.

The next three runs were to be used as an indication of the sensitivity of the apparatus. The various concentrations were made by injecting a known volume of EGDN vapor into the test chamber. The most dilute run was 1 part of EGDN in 3000 parts of air. This dilution gave a positive result. The retention time was 1.2 min, with a peak height of 8 divisions.

Figures 85, 86, and 87 show readouts for three experiments.

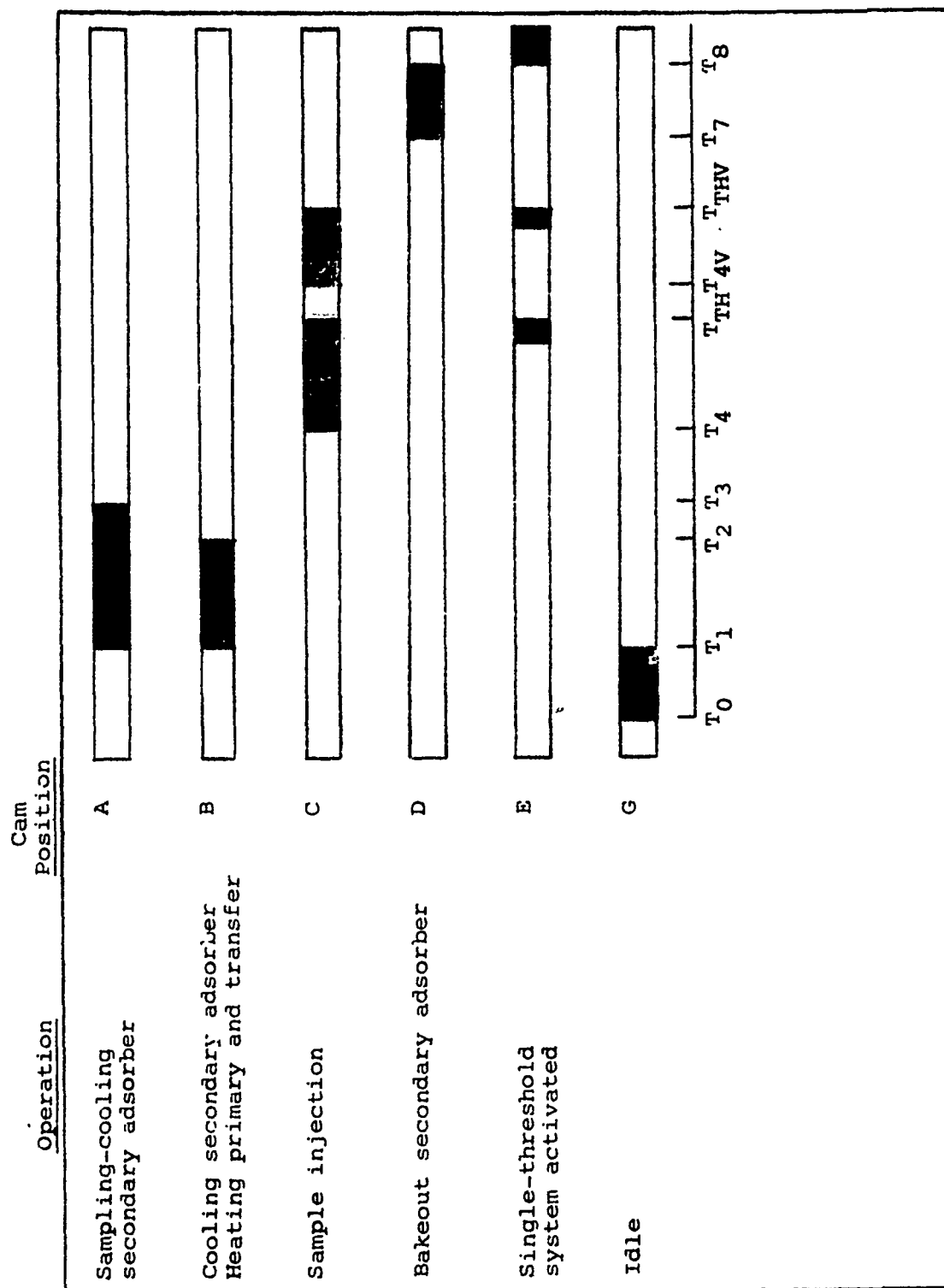


FIGURE 83 - Cam-Actuator Relationship

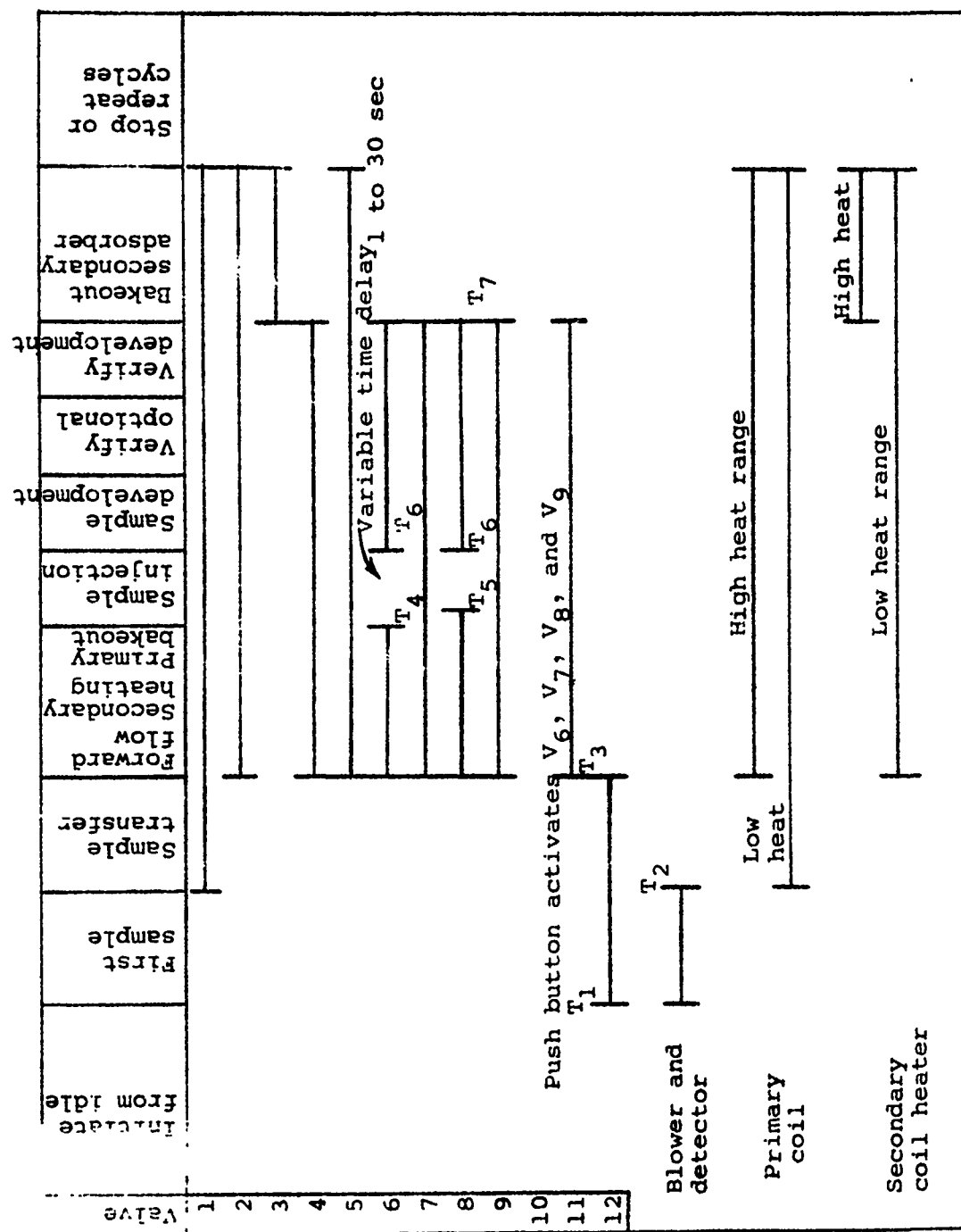


FIGURE 84 - Valve-Operation Relationship

TABLE XX - Detection of EGDN with the Engineering Model

Concentration	Sampling Time	Transfer Time, min	Transfer Rate, cfm	Retention Time, min	Height of Peak, divisions	Zero-Argon Carrier Gas Flow Rate, cc/min
10-sec exposure, open container at inlet of primary adsorber	10 sec	2	0.25	1.2	80	48
5-min exposure, open container in test chamber	1.5 min	2	0.25	1.2	85	48
1:1000	1.0 min	2	0.25	1.2	13	48
1:2000	1.0 min	2	0.25	1.2	6	48
1:3000	1.0 min	2	0.25	1.2	8	48

Volume of test chamber 3000 liters. All injections for 30-sec periods.



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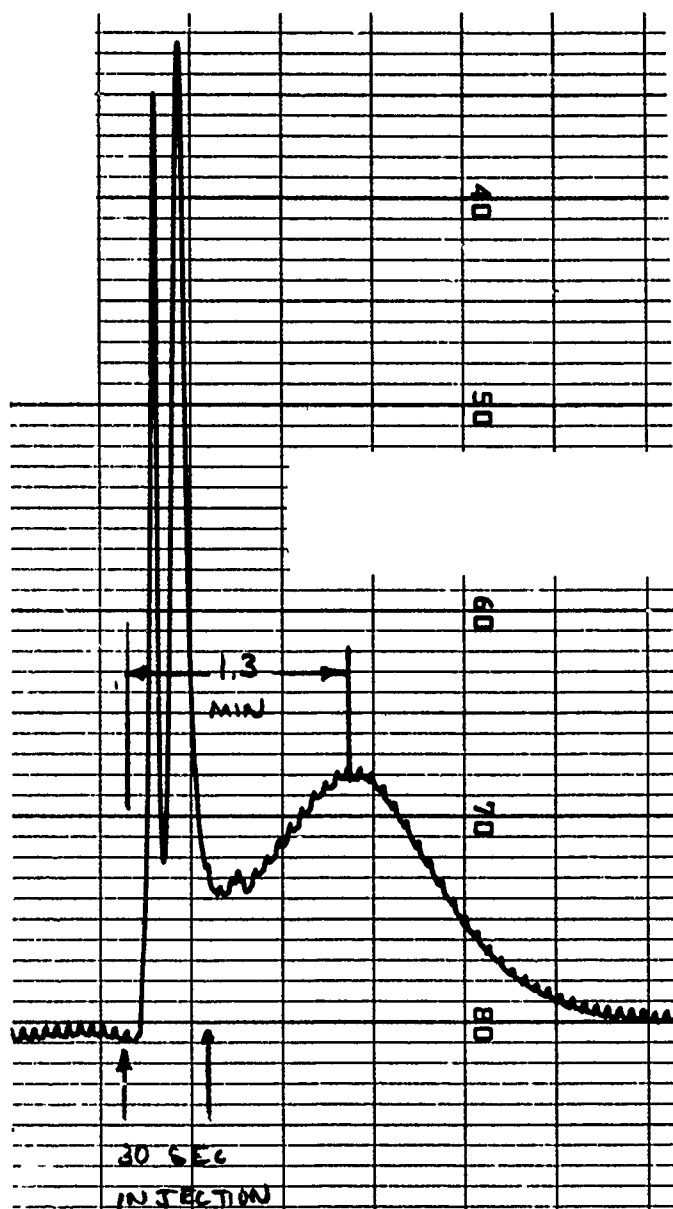


FIGURE 86 - Recorder Readout for EGDN Diluted 1:1000

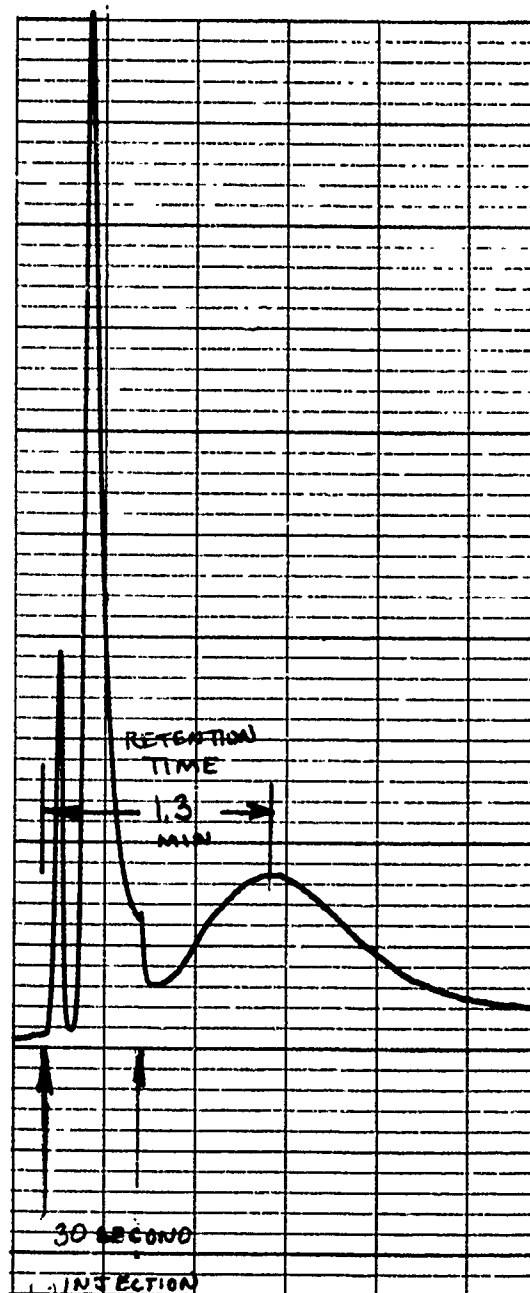


FIGURE 87 - Recorder Readout for EGDN Diluted 1:3000

These demonstrations indicated that the stages of the engineering model operate together in a proper manner and that the model detects dynamite. Some air and argon leakage in the sealing slip-surfaces of Teflon primary adsorber was observed and diminished the signal by loss of EGDN vapor during the transfer from the primary to the secondary adsorber. This mechanical problem is being corrected.

The time distribution in the demonstration runs is shown in Table XXI. Presently, the total cycle time is 5 min and 40 sec, but this can be shortened as more experience is gained.

Thus, although the experiments so far have been only under controlled laboratory conditions and moderate dilutions of the dynamite vapor, the operability of the engineering model has been demonstrated.

TABLE XXI - Time Cycles in the Engineering Model

Operation	Time
Sampling	60 sec
Transfer	120 sec
Heat secondary adsorber	40 sec
Injection	30 sec
Time for EGDN peak development	<u>90 sec</u>
	340 sec = 5 min 40 sec
Verify injection (optional)	30 sec
Time for EGDN peak development ^{Optional}	60 sec
Bakeout secondary adsorber	<u>70 sec</u>
With verify	500 sec = 8 min 20 sec
Without verify	410 sec = 6 min 50 sec

Thus, without optional verify, the unit can completely process one sample and be capable of processing another sample within 6 min and 50 sec.

5.0 CONCLUSIONS

1. Detection of dynamite via detection of the vapor of ethylene glycol dinitrate (EGDN) in air was achieved by a process in which EGDN vapor is adsorbed from air upon gold, released from the gold by heating to 80 to 90°C, and then, after passage through an Apiezon-L/Fluoropak partition tube at a controlled rate, detected by means of electron capture. Optimization of all components and operating parameters led to a process of very high sensitivity and permitted design and construction of an engineering model of the bomb detector.

2. The engineering model of the bomb detector can perform all operations, beginning with air sampling and ending with a readout, within several minutes. In this model, two vapor-transfer steps are needed, to permit collection from a large volume of air and analysis in a small, high-sensitivity system.

3. In bench-scale tests with manual transfer of samples, EGDN was still detectable in air at dilutions (from vapors equilibrated with dynamite) of 1:500,000 to 1:1,000,000, or approximately 0.1 to 1 parts per billion. The engineering model, equipped for automatic operation, demonstrated detection of dilutions of 1:3000. This level is sufficient for scanning of luggage, and it is being escalated by improvements in the rigidity of the primary vapor adsorber. These improvements will eliminate losses in vapor transfer from the primary to the secondary adsorber. Some acceleration of the vapor detection process is feasible.

4. Nitrobenzene vapor, which can originate from various solvents, is separable from EGDN vapor and should be detectable (for example, from plastic bombs) by a similar process.

5. No simple process was found promising for detection of black powder by characterization of its vapor, but the possibilities have not been exhausted.

6. A microwave absorption detector showed promise for very characteristic detection of dynamite but not of trinitrotoluene-type explosives. This detection method is not high sensitive and requires substantial advances in technology before it can be practical.

7. Microwave-heated plasma emission spectrophotometry shows promise as a very sensitive method, but the specificity for EGDN will be more difficult to attain than with the

electron-capture detector. The very high sensitivity of the plasma emission detector to nitrogen compounds in any form is the principal factor in this difficulty.

8. The selected process (gold adsorbers, short partition column, and electron-capture detector), demonstrated by the engineering model of the bomb detector, is thus far the most promising approach to detection of ethylene glycol dinitrate, which accompanies dynamite as well as self-made nitroglycerine and dynamite. It is easily adaptable to detection of nitrobenzene, which has been reported to accompany plastic bombs. Its adaptation to detection of trinitrotoluene- and dinitrotoluene-containing explosives will require considerable escalation of its capabilities.

6.0 RECOMMENDATIONS

Since optimization of the various steps in the dynamite detector resulted in an operating engineering model that has repeatedly detected dynamite in trial runs, we recommend that testing of the engineering model be continued concurrently with various improvements in the components and in the linking of the components. The testing should be conducted under increasingly difficult detection conditions, and the causes of limitations in the performance, if such occur, should be found and corrected at each difficulty level. The testing should gradually approach typical air terminal and airplane conditions.

We recommend that then a second model should be constructed. It should be based on the experience obtained with the present model but should be simplified and improved in every way possible, and particular attention should be given to those factors that facilitate the maintainability of the bomb detector.

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